Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 230 NOVEMBER, 1940 No. 5

# THE STEAM LOCOMOTIVE: ITS DEVELOPMENT AND PRESENT POSITION IN RAILROAD TRANSPORTATION.*

BY

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To present a paper on the Steam Locomotive in the City of Philadelphia may not be carrying coals to Newcastle, but it is rather like offering a course on colliery engineering in that Northumbrian city. To mitigate a charge of presumption, let me say that, though now an exile, my struggles with locomotive problems began at Broad and Spring Garden Streets.

My subject this evening is the Steam Locomotive: Its Development and Present Position in Railroad Transportation. I hope to show you something of the steam locomotive's history, to look briefly at its anatomy, to discuss some of the principles of its physiology, and to consider its present social standing.

A columnist in the Chicago *Daily News* for Nov. 9, 1939, expressed the opinion that "The three most romantic creations of man are: Schubert's songs; Chinese painting; and the American steam locomotive." I share his enthusiasm, but cannot offer to deal with the locomotive in this setting. All

* Presented at the Stated Meeting held Wednesday, February 21, 1940.

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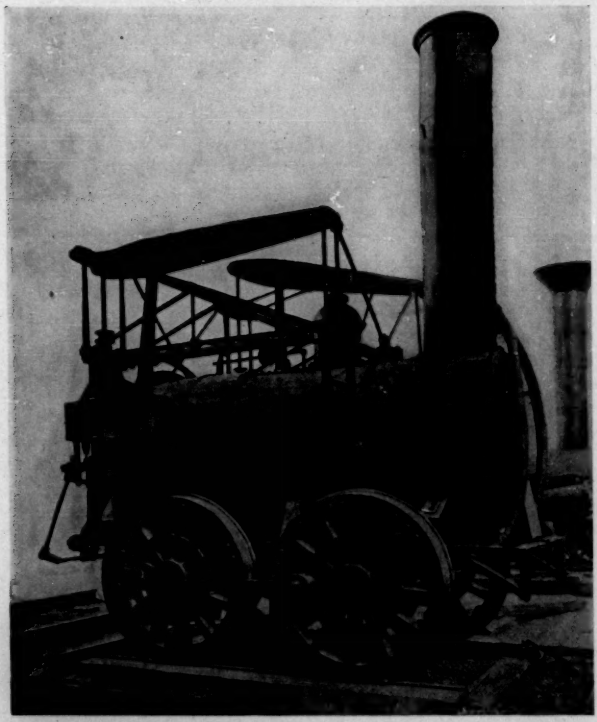
I can hope to do is to show you a most ingenious engineering job for which the original lines were laid down by George and Robert Stephenson in 1829. Its development along those lines has had a most profound influence on our country.

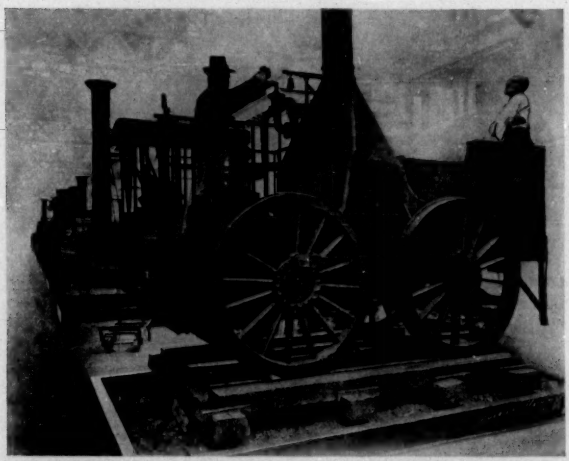
FIG. 1.



As an introduction to a more detailed study, I present a few representative locomotives that have run on the rails of this country in the last 110 years:

Figure 1 shows the "Stourbridge Lion," the first locomotive to run on an American railroad. It was bought of Foster and Rastrick of Stourbridge, England, by Horatio Allen for the Delaware and Hudson Canal and Railroad Company. It reached Honesdale, Pa., by canal boat. On August 8, 1829, it was under steam for its first trial trip. Mr. Allen (1) * knew that the wooden rails were cracked by the summer heat and that the 30-foot high trestle over the Lakawaxen Creek was none too strong for the heavy locomotive. However, the

FIG. 2.



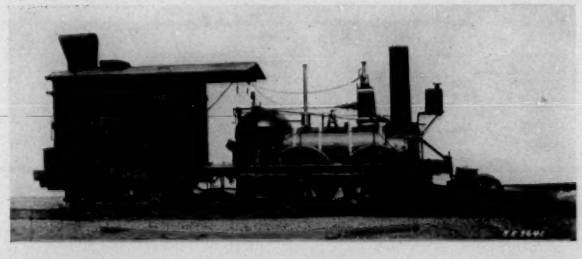
countryside had turned out to see the steam engine run. Horatio Allen took the throttle and announced that he would go alone. At first he thought of trying the trestle slowly, but finally, as he said later, he decided to at least go down handsomely, so started with considerable velocity, crossed the creek safely, and after running two or three miles returned to the starting place amidst the cheering of the people and the booming of cannon, having made the first railroad trip on the Western Hemisphere.

* Numbers in parenthesis refer to the bibliography.

Figure 2 is the "Best Friend," the first locomotive built in America for railroad service. It was put into service on the South Carolina Railway on Christman Day, 1830, "whisking" one hundred and forty-one passengers "on the wings of the wind at the varied speed of fifteen to twenty-five miles an hour," to quote the representative of the Charleston *Courier*. The "Best Friend" ran successfully without serious accident until June 17, 1831, when the Negro fireman, disliking the noise of the escaping steam, tied down the safety valve. This was the date of the first locomotive boiler explosion.

Figure 3 is the "John Bull." This locomotive claims several "firsts." It was bought in December, 1830, by Robert

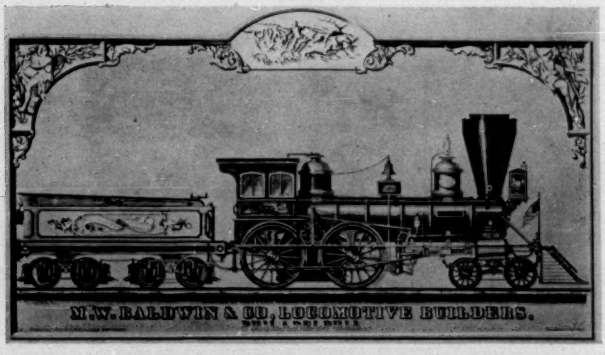
FIG. 3.



Stevens of Hoboken (2) from Robert Stephenson of Darlington, England, for the Camden and Perth Amboy Railroad and Transportation Company, which was chartered in 1815 and was the first link in what is now the Pennsylvania Railroad. The "John Bull" was the first American locomotive of the Stephenson design, a design which has served as the basic plan for steam locomotives ever since. Before being put into service, it was inspected by Mathias Baldwin and served as a pattern for the first railroad locomotive built in Philadelphia. As shipped from England, the locomotive had four wheels of the same diameter. Later the two front truck wheels shown in the Figure were added to help guide the locomotive around the sharp American curves.

In Fig. 4 we move along 25 years to "The Tiger," (3) a fast passenger locomotive weighing 30 tons, built by the Baldwin Locomotive Works in 1856 for the Pennsylvania

FIG. 4.

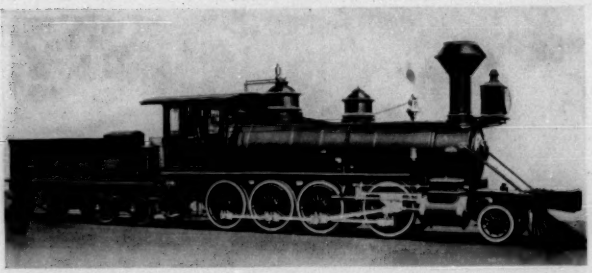



Railroad. The decorations of this period may be thought to verge on the rococo, but they do not hide the fine functional clarity of the design. All the elements are distinct, the boiler with its deep firebox between the wheels and its ample spark arresting smoke-stack; the cylinders with their controlling valve motion and the driving rods connecting the pistons direct to the wheels; all are plainly seen. The driving wheels are clearly marked as the elements of traction, while at the front is the pony truck carrying part of the weight of the boiler and serving as a guide in passing curves. With the exception of the truck, these are the elements put together by George and Robert Stephenson.

Figure 5 is a freight locomotive of about twenty years later, weighing 50 tons. Note that in place of the four driving wheels and four truck wheels of the "Tiger" passenger engine, the freight locomotive has eight driving wheels and two truck wheels. The larger number of driving wheels indicates a greater tractive effort or pull. The reduction in the number of truck wheels indicates that the boiler capacity is smaller

in relation to the tractive effort. The pull that a locomotive can exert is limited by the grip of the driving wheels on the rails. Roughly speaking, the pull cannot exceed about one-quarter of the adhesive weight, that is, of the weight carried

FIG. 5.



by the driving wheels. Therefore, when each pair of wheels carries the full weight allowed by the rail, an increase in tractive effort calls for an increase in the number of driving wheels.

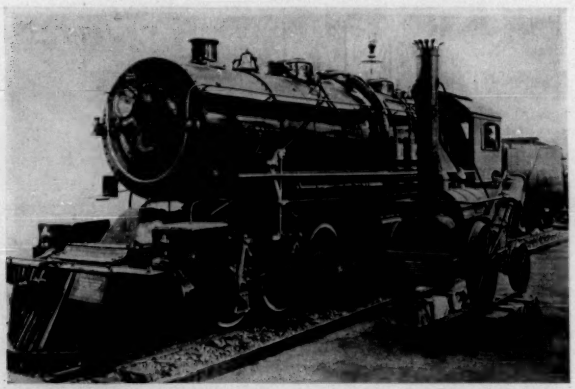
The speed, that is, the rate at which the driving wheels can be turned, depends on the rate at which the boiler can supply steam. For high speed the boiler must be large, and its weight becomes greater than is needed for adhesive weight. Additional carrying wheels in the form of truck or trailer wheels are then added. Locomotives for a slow, heavy drag have many drivers and a minimum of carrying wheels, while locomotives for less pulling capacity but higher speeds have fewer driving and more carrying wheels.

The consolidation engine shown was a powerful freight locomotive in its day. I have a report dated December 27, 1877 (4), made by my father, Howard Fry, then Superintendent of Motive Power of the Philadelphia and Erie Division of the Pennsylvania, which shows that a consolidation locomotive similar to that of Fig. 5 was hauling 100-car trains between Sunbury and Harrisburg. Train weights were about 2400 tons behind the tender, and the running time for the 46

miles was about three hours and twenty minutes. Many of you will, I think, agree that to handle a train of this length with link and pin couplings and hand brakes must have required skillful work by the engineman.

Figure 6 from a picture, taken at the St. Louis Exposition, brings us ahead to 1904 with the Baltimore and Ohio Mallet

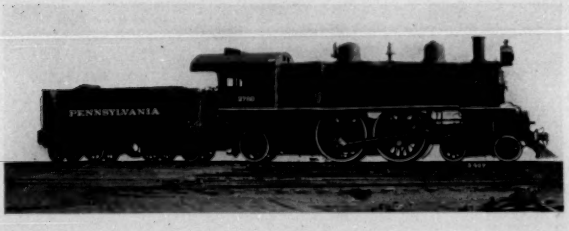
FIG. 6.



compound and takes us back to 1829 with the replica of Stephenson's "Rocket." In the other pictures showing the earlier locomotives standing by themselves, we are able to think of them, as their builders did, as being powerful machines. In this slide the "Rocket," weighing four and one-quarter tons, is dwarfed by the 168-ton B. and O. engine. This latter follows an arrangement first used by Anatole Mallet in France on much smaller engines. It comprises two engines under a single boiler. The steam is admitted first to the rear cylinders and after a preliminary expansion there is carried forward to the front cylinders for further expansion. This double expansion is the so-called "compounding" which is discussed later. The front engine frame is hinged to the rear frame so that it can swing under the boiler to pass around curves.

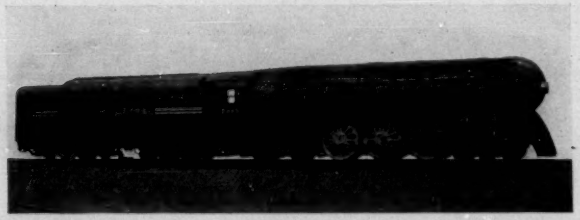
Figure 7 shows an Atlantic type passenger locomotive of 35 years ago. The weight is about 93 tons, and to carry the

FIG. 7.




boiler required for high speeds a pair of trailing wheels and a four-wheeled front truck are provided. The next illustration, Fig. 8, shows another powerful passenger engine, but of the

FIG. 8.



present time. This locomotive is the New York Central streamlined Hudson type locomotive. This engine weighs about 183 tons, or practically twice that of the Atlantic type of 35 years ago, Fig. 7. Greater tractive effort is indicated by the use of six instead of four driving wheels. The eight truck wheels to six driving wheels indicates an ample boiler designed for high speed. This locomotive has hauled a 1000-ton train at 90 miles per hour.

Figure 9 closes this introduction with a modern heavy freight locomotive. This Norfolk & Western Mallet weighing 360 tons is one of the heaviest locomotives in existence.

Having noted briefly the growth of the steam locomotive, I offer some figures to show the improvement in operating efficiency which has come with this growth. The figures in

FIG. 9.

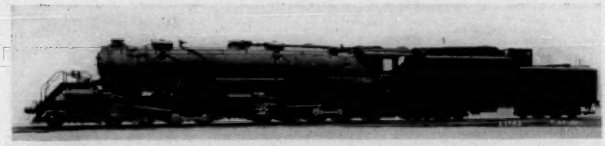


Table I show two things: First, that transportation has moved off the rails; second, that the steam locomotive is growing in power and efficiency. The figures in Table I are taken from

TABLE I.

*From 1939 Report of A. A. R. Joint Committee on Utilization of Locomotives and Conservation of Fuel*

Freight Service.

| 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|---|---|---|---|---|---|---|
| Year. | Business Handled. | Equipment Used. | Loading. | Speed. | Achievement. | Cost. |
| | Million Ton Miles. | No. of Locos. Serviceable. | Tons per Train. | Miles per Hour. | Ton Miles per Train Hour. | Pounds of Fuel per 1000-Ton-Mile. |
| 1920..... | 914,940 | 23,731 | 1,443 | 10.3 | 14,877 | 197 |
| 1938..... | 794,428 | 16,850 | 1,895 | 16.6 | 31,138 | 132 |
| Per cent. Change... | −13.0 | −29.0 | +31.3 | +61.0 | +109 | −34.0 |

Passenger Service.

| | Million Car Miles. | No. of Locos. Serviceable. | Cars per Train. | Train Miles per Day. | Car Miles per Loco. per Day. | Pounds of Fuel per Car Mile. |
|---|---|---|---|---|---|---|
| 1920..... | 3,584 | 10,318 | 6.44 | 144.2 | 910.2 | 18.8 |
| 1938..... | 2,688 | 6,140 | 7.91 | 168.9 | 1335.1 | 15.8 |
| Per cent. Change... | −25.0 | −40.5 | +22.8 | +17.1 | 46.7 | −16.0 |

the 1939 report of the Association of American Railroads Committee on the Utilization of Locomotives and Conserva-

tion of Fuel. They are based on reports from 60 Class 1 railroads; that is, roads with incomes of more than one million dollars a year. I give the figures for the years 1920 and 1938, not because of special characteristics of these years, but because they illustrate the twenty-year trend.

In freight service the ton-miles of business offered have fallen off 13 percent., but the number of locomotives used has been reduced 29 per cent. The locomotives are stronger and are more efficiently used. The weight of each train has gone up 31 per cent. and the speed has been increased 61 per cent. In spite of this increase in speed, the fuel per 1000 ton-miles has been reduced 34 per cent.

In passenger service the story is the same. With a reduction of 25 per cent. in passenger-car miles, the number of locomotives has been cut 40 per cent. Each locomotive delivers 46 per cent. more car-miles per day with 16 per cent. less fuel per mile. I do not want statistics to raise its nasty head too far, so we pass on, but the figures show that in the face of declining business railroaders and their locomotives continue to show an increase in efficiency.

For our further and more detailed study of the steam locomotive, I take a text from Alexander Pope. In the introduction to his Essay on Man he says:

> "To examine the perfection or imperfection of any creature whatsoever, it is necessary first to know what condition and relation it is placed in, and what is the proper end and purpose of its being."

The "proper end and purpose" of the steam locomotive is to produce transportation of goods and passengers with speed and economy. On that basis it must stand or fall. Mechanical efficiency alone is not enough. As A. M. Wellington has said (5), "An engineer is one who can do well for one dollar that which any bungler can do badly for two!"

The "condition and relation" of the steam locomotive is that in railroad service it is in competition with electric locomotives and with the newer Diesel-electric locomotives. Electric locomotives first came into service in the tunnels under Baltimore and New York where smokelessness was important. Their use grew in the dense traffic areas radiating from New

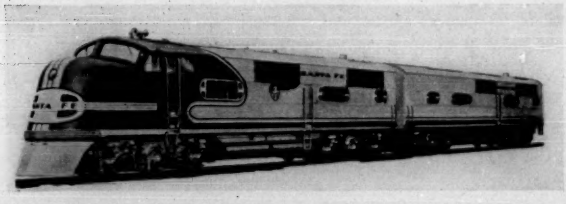
York and Philadelphia. At the present time the roads out of New York City are electrified to Harmon 32 miles out on the New York Central, and to New Haven 72 miles out on the New York, New Haven & Hartford. On the Pennsylvania the electric wires run from New York to Washington, 227 miles, and from Philadelphia to Harrisburg, 114 miles. Fig. 10 shows one of the latest high speed electric locomotives of the Pennsylvania Railroad.

FIG. 10.

Mechanically speaking, the electric locomotive is a more highly specialized machine than the steam locomotive. The steam locomotive generates its own power and, carrying its own supply of fuel and water, is free to travel any tracks so long as this supply lasts. The electric locomotive turns into mechanical work the vital electric fluid received from the transmission lines. It operates only when backed up by large stationary power plants and an intricate system of power transmission. Like other highly specialized organisms, the electric locomotive has a limited possibility of existence. The first cost of the transmission system is so high that the overhead charges can be carried economically only if the traffic is dense. The financial load of each mile of transmission equipment must be carried by a large number of trains per day.

Competition from the Diesel-electric locomotive is of a different order. No expensive transmission lines are required. Fig. 11 shows a modern Diesel-electric locomotive. Each

FIG. 11.



locomotive is a self-contained travelling power plant, so that it is subject to no more limitations than the steam locomotive. In fact, the Diesel is freer, because it does not need a supply of specially prepared water available at intervals along the line.

A mechanical study of the Diesel-electric locomotive is outside of the scope of tonight's paper, but a brief comparison with the steam locomotive is desirable to evaluate the "condition and relation" in which the steam locomotive stands.

Both machines burn fuel to produce heat, and use cylinders and pistons to turn the heat into work which makes the wheels go round. The difference between the two lies in the operations by which the heat units of the fuel are converted into mechanical work at the wheels.

In the steam locomotive the fuel burns in the firebox; and the transfer of the heat to the cylinders requires the use of boiler, water, steam, superheater, and steampipes.

In the Diesel all this heat transfer apparatus is unnecessary. The fuel burns in the cylinders and its heat is turned directly into work at the pistons. However, this advantage is offset by the complication necessary to transfer the work from pistons to driving wheels. In the Diesel the pistons drive a generator which sends electricity through the controllers to drive motors which drive the wheels through gearing. The steam pistons act directly on the driving wheels through the rods.

The first cost of the Diesel is higher, but this can be offset by making it work longer hours. In a recent paper on High Speed Trains, Mr. C. T. Ripley offers a well documented study of the two types of locomotives. He finds that the total cost of operation is about the same for both.

The rise to prominence of the Diesel-electric locomotive in passenger service seems to be due to one part progressive engineering mixed with at least one part of forceful salesmanship. The challenge has, however, spurred the steam builders; and their recent productions compete with the Diesels on equal terms, both mechanically and as to eye-appeal. It seems probable that if this energy had been shown a little earlier the labor-pains with which the Diesel was brought into the world would have been more severe.

I now close this survey of the competitive situation and direct attention to the development of the steam locomotive. This development has been persistent since the embryo "Rocket" was fathered 110 years ago. Many eminent engineers and many farsighted and hard-headed business men have been essential factors, but I think that attention may well be called to two family groups, with a father and a son in each, who had an essential part in determining the course which development has followed. The Stephensons in England established the basic locomotive design which has been standard for over a hundred years, while the Stevens brought this design to America.

George Stephenson (1781–1848) and his son, Robert (1803–1859), were of great importance as engineers in building the first English railways and in developing the locomotives to operate them. John Stevens of Hoboken (1749–1838) was among the earliest and most enthusiastic railroad promoters in America and with his son Robert (1787–1859) contributed to locomotive engineering by building a model locomotive in 1825, the first to run on rails in America, and by the importation in 1831 of a Stephenson locomotive.

In England at the beginning of the nineteenth century the industrial revolution was well under way. James Watt's steam engines were in common use, coal mining was an important industry, and heavy manufactures were growing. Transportation was a necessary factor in this growth. Many

canals had been built, and were proving profitable, and some of the more important coal mines had rail-ways designed originally for horse traction. It was natural for the colliery engineers, who were using steam engines for pumping, to try to apply steam to traction.

In this application George Stephenson took a notable part. He was a self-taught genius, who began work at the age of eight. He did not learn to read and write until he was eighteen, but at twenty-two he was superintendent engineer of the important Killingworth Collieries. This was in 1803, and eleven years later in 1814 George Stephenson built his first locomotive for colliery service. In the next eleven years eleven more locomotives were built to Stephenson's designs. By that time, though, that is in 1825, there were only 18 locomotives at useful work in England and only a few enthusiasts thought they had any future (6).

In America, however, that very early enthusiast, John Stevens of Hoboken, was seeing visions. In 1812, two years before Stephenson's first locomotive, Stevens published a pamphlet, "Documents tending to Prove the Superior Advantages of Railways and Steam Carriages over Canal Navigation." Considering the embryonic state of the steam carriages at the time, this seems like sheer prophecy unhampered by facts. However, Wisdom was justified of her child.

John Stevens, a Major in the Revolutionary War, had established an estate at Castle Point, Hoboken. Without mechanical training, he became interested in the application of steam to marine and land transportation. He developed a steamboat and for many years fought bitterly against Fulton's exclusive rights to operate steamboats on the Hudson River. He also petitioned the state legislatures for charters for steam railroads. On February 6, 1815, the legislature of New Jersey granted to John Stevens and his associates a charter for the Camden and Perth Amboy Railway and Transportation Company. Eight years, later, March 21, 1823, after several months of intensive lobbying in Harrisburg, Stevens obtained from the legislature of Pennsylvania a charter for the Pennsylvania Railroad to run between Philadelphia and Columbia. These two charters mark the beginning of the present Pennsylvania Railroad System.

In England the development of railroads had made more definite progress. Stationary steam engines were numerous, industry was more advanced, and the necessary capital more plentiful. The first public railway was the Stockton and Darlington, projected in 1821 for haulage of merchandise and opened in 1825 with two of George Stephenson's steam locomotives as motive power. The "Quaker Line," as it was nicknamed because many of its Directors belonged to the Society of Friends, was successful from the first. Its novelty and the very satisfactory earnings aroused interest throughout Europe and the United States.

The next important road to be opened was the Liverpool and Manchester, the first of the railways, as we know them, intended for passengers as well as goods. With George Stephenson as engineer, the road was built as a substantial civil engineering work before a definite decision was made as to whether the cars should be hauled by horses, stationary winding engines, or by locomotives. This permanent construction had the disadvantage of freezing the loading gage and hampering the growth of the rolling stock.

George Stephenson was a strong advocate of steam locomotives, and finally the Directors decided to offer a prize of 500 pounds for the most suitable locomotive, capable of hauling three times its own weight at a speed of not less than 10 miles an hour.

The interest aroused by the competition is shown in the following contemporary account (7):

> "Multifarious were the schemes proposed to the Directors for facilitating Locomotion. Communications were received from all classes of persons; from professors of philosophy down to the humbliest mechanic; England, America, and Continental Europe were alike tributary. The friction of the carriages was to be reduced so low that a silk thread would draw them, and the power to be applied was to be so vast as to rend a cable asunder. Hydrogen gas and high pressure steam—columns of water and columns of mercury—a hundred atmospheres and a perfect vacuum—wheels within wheels to multiply speed without diminishing power—to the ne plus ultra of perpetual mo-

tion. Every scheme which the restless ingenuity or prolific imagination of man could devise was liberally offered to the Company; the difficulty was to choose and decide."

The competition for the prize was set for October 6, 1829. The contest appealed to the public as a sporting event and drew a large crowd. The Liverpool *Courier* for October 7, 1829, gave the following account:

> "The Directors of the Liverpool and Manchester Railroad having offered, in the month of April last, a prize of 500 pounds for the best Locomotive Engine, the trial of carriages which had been constructed to contend for the prize commenced yesterday near Rainhill bridge. The directors had made suitable preparations for this important experiment of the powers of Locomotive Carriages. For the accommodation of the ladies who might visit the course a booth was erected, and here a band of music was stationed, and amused the company during the day. The directors, each of whom wore a white ribbon in his buttonhole, arrived on the course shortly after ten o'clock in cars drawn by Mr. Stephenson's Locomotive Steam Carriage. The spectators lined both sides of the road for the distance of a mile and a half, to the number of not less than 10,000.
>
> "Never, perhaps, on any previous occasion, were so many scientific gentlemen and practical engineers collected together in one spot as there were on the Railroad yesterday. The interesting and important nature of the experiments to be tried had drawn them from all parts of the kingdom."

Five competitors had entered their names, but only three locomotives were ready for the competition. The "Novelty" by Braithwaite and Ericsson (who later designed the Monitor) was the popular favorite, but could not make enough steam. Burstall's "Perseverance" was a slow, clumsy colliery type of locomotive like the "Stourbridge Lion" of our Figure 1. The successful competitor was Stephenson's "Rocket."

Before following the development of the design established by the "Rocket," I should like to show you the Liverpool and Manchester Railway as it reached completion.

For an account of the road I quote an entirely untechnical, but very acute observer, Miss Fanny Kemble, the actress. She had made her first and tremendously successful appearance just about a year before. While acting at Liverpool, she and her father were invited to accompany some of the proprietors of the Liverpool and Manchester Railway on an experimental trip. This was about three weeks before the opening, and Miss Kemble's letter of August 26, 1830, gives an interesting picture of the railway as she saw it:

"And now I will give you an account of my yesterday's excursion. A party of sixteen persons was ushered into a large court-yard, where, under cover, stood several carriages of a peculiar construction, one of which was prepared for our reception. It was a long-bodied vehicle with seats placed across it back to back. The wheels were placed upon two iron bands, which formed the road. The carriage was set in motion by a mere push and rolled with us down an inclined plane into a tunnel, which forms the entrance to the railroad. This tunnel is four hundred yards long (I believe) and will be lighted by gas. At the end of it we emerged from darkness and, the ground becoming level, we stopped.

"Here we were introduced to the little engine which was to drag us along the rails. She (for they make these curious little fire horses all mares) consisted of a boiler, a stove, a platform, a bench, and behind the bench a barrel containing enough water to prevent her being thirsty for fifteen miles. She goes upon two wheels, which are her feet, and are moved by bright steel legs called pistons; these are propelled by steam, and in proportion as more steam is applied to the upper extremities (the hip-joints, I suppose) of these pistons, the faster they move the wheels; and when it is desirable to diminish the speed, the steam, which unless suffered to escape would burst the boiler, evaporates through a safety valve into the air. The reins, bit, and bridle of this wonderful beast is a small steel handle, which applies or withdraws the steam from its legs or pistons, so that a child might manage it. The coals, which are its oats, were under the bench, and there

was a small glass tube affixed to the boiler, with water in it, which indicates by its fullness or emptiness when the creature wants water, which is immediately conveyed to it from its reservoirs. This snorting little animal, which I felt rather inclined to pat, was then harnessed to our carriage, and Mr. Stephenson having taken me on the bench of the engine with him, we started at about ten miles an hour.

"The steam horse being ill adapted for going up and down hill, the road was kept at a certain level, and appeared sometimes to sink below the surface of the earth and sometimes to rise above it. Almost at starting it was cut through the solid rock which formed a wall on either side of it, about sixty feet high. You can't imagine how strange it seemed to be journeying on thus, without any visible cause of progress other than the magical machine, with its flying white breath and rhythmical, unvarying pace, between these rocky walls, which are already clothed with moss and ferns and grasses."

After describing the passage through the Olive Mount cutting, the crossing of Chat Moss, and a walk with George Stephenson down into the valley spanned by the Sankey Viaduct, Miss Kemble proceeds:

"We then rejoined the rest of the party, and the engine having received its supply of water, the carriage was placed behind it, for it cannot turn, and was set off at its utmost speed, 35 miles an hour, swifter than a bird flies (for they tried the experiment with a snipe). You cannot conceive what that sensation of cutting the air was; the motion is as smooth as possible, too.

"Four years have sufficed to bring this great undertaking to an end. The railroad will be opened upon the fifteenth of next month. The Duke of Wellington is coming down to be present on the occasion, and, I suppose, that with the thousands of spectators and the novelty of the spectacle, there will never have been a scene of more striking interest. The whole cost of the work (including the engines and carriages) will have been eight hundred and thirty thousand pounds; and it is already worth

double that sum. The Directors have kindly offered us three places for the opening, which is a great favour, for people are bidding almost anything for a place, I understand."

The opening ceremony took place on September 15, 1830. The Duke of Wellington was present, and a contemporary account of the opening describes the Duke's carriage:

"This carriage was truly magnificent; its appearance was imposing and its workmanship was perfect and tasteful; superb grecian scrolls and balustrades, richly gilt, supported a massy handrail running round the carriage while ascending from it were gilded pillars, maintaining a canopy twenty-four feet long. The drapery was of crimson cloth and the whole surmounted by a Ducal coronet."

Back of all this pomp and ceremony stood the engineering genius of the Stephensons. Progress in locomotive development was rapid; a year after the four and one-quarter ton "Rocket" the Liverpool and Manchester put into service the "Planet," weighing eight tons. This locomotive is of particular importance in American locomotive history. Its official trial took place on December 4, 1830, when it took 18 waggons of a total weight of about 80 long tons from Liverpool to Manchester 31 miles in two hours and 54 minutes with three stops. An interested spectator was Robert Stevens, son of John of Hoboken, whose prophecies were now being fulfilled. Robert Stevens was in England to buy a locomotive for the Camden and Perth Amboy Railroad, which, as we have noted, was authorized 15 years earlier. Two days after the trial of the "Planet," Robert Stevens and Robert Stephenson agreed on the specifications for a locomotive along the lines of the "Planet." This locomotive, Fig. 3, which we know as the "John Bull," was shipped to the United States in March, 1831. It embodied the most advanced Stephenson design and by an interesting chance had an immediate and very definite influence on American locomotive engineering.

While the "John Bull" was in the receiving warehouse at Bordentown, it was examined by Mathias Baldwin of Philadelphia, who at that time had received an order for his first

full sized locomotive. It is of record that Mr. Baldwin looked over the "John Bull" carefully and made certain measurements. That Mr. Baldwin knew a good thing when he saw it is evident. "Old Ironsides," which he built that year for the Philadelphia, Germantown and Norristown Railway, is definitely of the Stephenson strain. Mr. Baldwin was an ingenious mechanic who developed later into a great locomotive designer and builder, but his inspection and sincere flattery of the "John Bull" undoubtedly saved him much grief in his first attempt. "Old Ironsides" went into service in November, 1832, the first of over 62,000 locomotives to be built in Philadelphia.

To understand the importance of "John Bull's" contribution to American railroading, we must realize that no locomotive built in America at that time, except "Old Ironsides," has left any traceable effect on our present practice. It has been said (8) that the functional elements used by the Stephensons were not new. This is largely true, but the arrangement of these elements was so masterly that it has persisted for 110 years. This arrangement is shown in Fig. 12, taken from Pambour's treatise on the locomotive engine, published in 1840. The drawing serves to illustrate the basic design used by locomotive builders today.

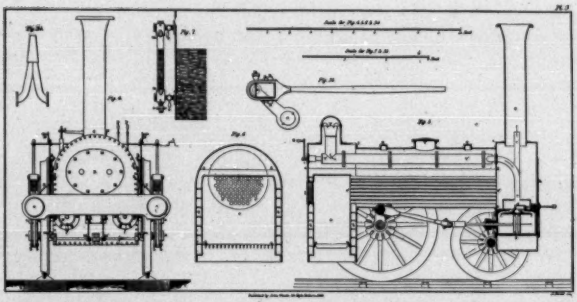
The problems of the steam locomotive are to burn the fuel to produce heat, to use the heat to turn water into steam, and to use the steam in the cylinders to make the wheels go round.

Fig. 12 shows the Stephenson solution of these problems. The fuel is burned in an approximately cubical firebox, surrounded by water except at the fire door and the grate. There is no free escape for the radiant heat of the fire; it must go to the water. The gases of combustion are carried off through a number of flues of small diameter. This was probably Séguin's idea, passed on to the Stephensons by Henry Booth, but Séguin failed to make it work and the Stephensons succeeded. By using tubes of small diameter, the hot gases escaping from the fire are never far from the tube surface in contact with the water and therefore give up their heat rapidly and efficiently.

The cylinders are set horizontally with the pistons connected directly to the driving axle by the piston rods and

connecting rods. Last and very much not least is the arrangement by which the steam after having done its work, in the cylinders is exhausted up the smokestack. The exhaust steam carries with it the gases from the smokebox and thus draws through the fire the air required for combustion. Sufficient air supply is of great importance. To burn a ton of coal about 10 tons of air must be put through the firebox. A ton of air will fill about 8 box cars, so that a modern locomotive burning 5 tons of coal an hour would require 400 box cars to carry an hour's supply of air. It is fortunate that the supply of air is free and universal.

FIG. 12.



The Stephenson arrangement gives the so-called "linked triangle of fire, air, and water" (9) which is fundamental in the physiology of the locomotive. The work to be done requires steam, and as the steam escapes through the stack, it draws air through the grate to stimulate the fire. To do more work requires more steam, which produces more draft, which forces the fire to produce more steam. The arrangement is as automatic as the old lady getting her pig over the stile. This cycle remains the basis of locomotive operation today in spite of the great increase in dimensions and considerable improvement in efficiencies.

Improvement in boiler efficiency has been helped by better knowledge of the processes involved. As early as 1835 Compte de Pambour (10) described locomotive boiler tests

showing that the boiler efficiency dropped as the boiler output was increased. At a firing rate of 112 pounds of coke per hour, each pound of coke evaporated 7 pounds of steam. When the firing rate was increased to 715 pounds per hour, the evaporation was only 5 pounds of steam per pound of coke. The same effect is observed today, but the exact reasons for it were not known until about 25 years ago. It was known that as the boiler was forced, more unburnt coal was thrown out of the stack, and that at the same time the temperature of the smokebox gases increased. It was, therefore obvious that the drop in boiler efficiency was due to more heat being lost up the stack. Many experiments had shown just how much heat was lost, but no tests had been so analyzed as to determine whether the greatest loss was due to incomplete combustion of the fuel or to failure of the boiler to absorb the heat produced. This question was first answered in 1907 by using the data obtained on the Pennsylvania Railroad locomotive testing plant in 1904. In this plant the locomotive can be run at any desired speed and power while measurements are made under laboratory conditions. The plant, after operating at the St. Louis Fair in 1904, was reërected at Altoona. Its most fruitful period of work began when my friend, Mr. C. D. Young, was appointed Engineer of Tests in 1911.

The Pennsylvania locomotive testing plant provided the necessary data for complete study of the locomotive boiler, but a method of interpretation had to be developed. In a stationary boiler plant the problem is simple. The gas analysis tells us the amount of gas produced by each pound of coal burned and the amount of coal burned is the amount fired less the ash pan losses. Knowing the weight and the temperature of the gases, it is a simple matter to calculate the amount of heat carried up the stack by the gases. In the locomotive boiler the method fails because the amount of coal actually burned is not known. Even with a locomotive on a stationary testing plant it is practically impossible to collect and measure all of the coal which escapes through the stack unburnt. Not knowing how much coal is actually burned, we do not know the total weight of gases of combustion and cannot find directly the amount of heat carried away by these gases.

In 1907 your speaker devised an indirect method of computation which has since been simplified. From the gas analysis we find the weight of gases produced for each pound of coal actually burned. Then, knowing the smokebox temperature, we know the heat carried away by the gases for each pound of coal burned. The difference between this and the heating value of the coal is the heat which has been taken up by the boiler for each pound of coal actually burned. The total amount of heat taken up by the boiler can be measured, and this divided by the heat taken up per pound of coal burned gives the weight of coal actually burned (11). By comparing the weight of coal burned with the weight fired, the efficiency of combustion is found.

Put in this form the method sounds rather obvious, but your speaker did not develop it until after a lot of hard work with the Pennsylvania test data. The method of computation in its first form was presented to the Institution of Mechanical Engineers in March, 1908 (12), together with the first complete accurate heat balances for a locomotive boiler. Since then this method, and no other is yet available, has been used to study locomotive boiler efficiencies. It has been found that the efficiency of heat absorption is affected very little by the rate at which the boiler is driven and does not vary greatly between one boiler and another. Practically any locomotive boiler of reasonable design will take up between 82 and 85 per cent. of the heat produced in the firebox. The over-all efficiency of the boiler is mainly determined by the efficiency of combustion, which falls off rapidly as the rate of combustion is increased. This is due to the difficulty of burning large quantities of coal in a firebox of limited size. When we start to crowd things, more and more coal is carried out of the firebox before it has time to burn. The amount thus lost may range from one or two per cent. at low rates of operation up to a loss of forty per cent. or more of the coal fired at an extremely high rate of firing.

For this reason improvement in locomotive boiler design requires adequate provision for proper combustion, rather than an undue increase in heat absorbing capacity.

It is, however, important to be able to estimate the effect of changes in the number, length, and diameter of the flues.

When one knows the answer, it seems fairly obvious that hot gas flowing through a tube surrounded by water will give up its heat more quickly if the diameter of the tube is small, and that more heat will be given up the longer the tubes and the greater the rate at which the gas is flowing. The general truth of these statements was established by early tests, but exact evaluation of the various factors is another matter. One of the speaker's greatest satisfactions came from the development of a formula enabling the temperature drop along a boiler flue to be computed from the flue dimensions and the rate of gas flow (13). If the flue has a mean wall temperature of $t$ and if the gas in flowing $x$ feet along the flue drops from a temperature $T_1$ to a temperature $T_2$, the relation between these temperatures is

$$\text{lolog } T_1/t - Mx = \text{lolog } T_2/t,$$

where the temperatures are measured in absolute units and $M$ is a coefficient derived from the equation

$$\log M = B - m \log W/p,$$

where $W$ is the rate of gas flow in the flue in pounds per hour.
$p$ is the gas swept perimeter of the flue in inches.
$B$ and $m$ are constants for any flue which are dependent only on the ratio of $a$, the area of the flue, to $p$, its gas swept perimeter. Values of $B$ and $m$ for various values of the ratio $p/a$ are given in reference (13).

One conclusion that can be drawn from the formula is that if 25 per cent. of the flues are stopped up, the increase in the rate of gas flow through the remaining flues will increase the rate of heat transfer so greatly that the amount of heat taken out of the gas will be only two or three per cent. less than that absorbed by the original number of flues (13), (14).

As a result of the knowledge accumulated from experiment and experience, locomotive power and efficiency have been increased as shown in Table II. A Stephenson Planet type locomotive in 1831 weighed about 10 tons and developed about 50 horsepower; that is, 5 horsepower per ton of locomotive

TABLE II

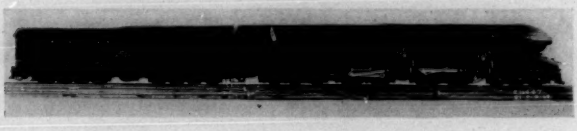
*Horsepower Developed per Ton of Locomotive Weight by Representative Locomotives at Various Periods.*

| Year. | Loco. | Class. | Type. | Locomotive Weight Tons (2000 lb.). | Indicated Horsepower. | |
|---|---|---|---|---|---|---|
| | | | | | Total. | per Ton. |
| 1831 | Planet type | | 2–2–0 | 11 | 50 | 4.5 |
| 1904 | P.R.R. | E2a | 4–4–2 | 93 | 1200 | 13.0 |
| 1914 | P.R.R. | K4s | 4–6–2 | 155 | 3300 | 21.4 |
| 1938 | N.Y.C. | J-3 | 4–6–4 | 183 | 4600 | 25.0 |
| 1937 | P-O | 240 | 4–8–0 | 120 | 3700 | 31.0 |

weight. By 1904 the horsepower per ton had increased to 13, while today the New York Central J3 weighing 183 tons develops 4600 horsepower, which is very nearly 25 horsepower per ton.

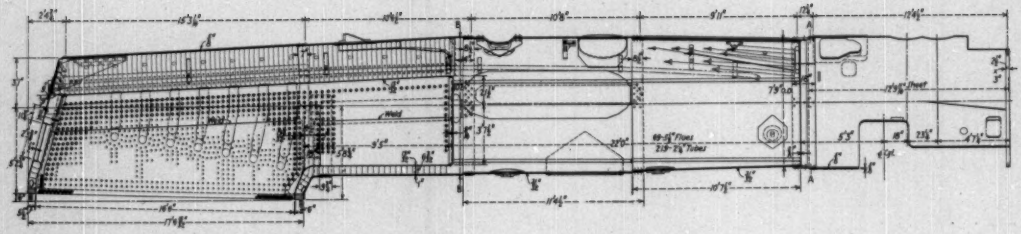
This increase through the years is in part due to better boiler performance, but even more must be attributed to bet-

FIG. 13.



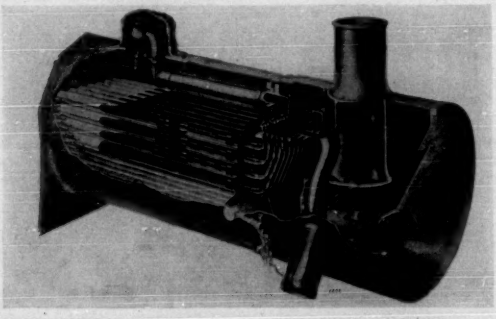
ter use of the steam in the cylinders. To examine this side of our subject, we must look at some modern locomotives. From the Planet type locomotive of 1840 we turn to the Pennsylvania Railroad S–1 locomotive of 1939. This locomotive, shown in Fig. 13, was exhibited by the Association of American Railroads at the New York World's Fair last year. It weighs 304 tons to the Planet's 10, and externally is very different. The four pairs of driving wheels indicate that a large tractive effort is to be developed. In addition, there are six pairs of truck and trailing wheels, indicating carrying capacity for a boiler to develop plenty of steam for high speeds. The locomotive is designed to haul 1200-ton passenger trains at 100 miles an hour.

FIG. 14.



A longitudinal section of the boiler is shown in Fig. 14. The basic functional elements are exactly the same as were seen in the Planet boiler of Fig. 12. The water enclosed firebox is at the rear as before, althouth the proportions have changed. The firebox with its combustion chamber extension has grown more in length than in the other directions. This is because of the restriction placed on over-all height and width by tunnels, bridges, and stations. From the firebox the flues, of which only two are shown, lead forward to the smokebox. So far the Planet design is repeated. In the modern locomotive a superheater is added. The flue bundle, not shown in Fig. 14, consists of 219 $2\frac{1}{4}$-inch flues and 69 $5\frac{1}{2}$-inch superheater flues. The general arrangement of the superheater is shown in Fig. 15. The steam is carried from

FIG. 15.

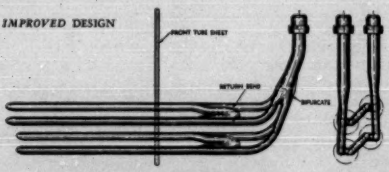


the boiler to the cylinder through a number of pipes $1\frac{1}{2}$ inch in diameter, each of which enters a superheater flue at its front and runs back nearly to the firebox, comes back to the front, and then repeats the route. This is the older, or Type A superheater. Many modern locomotives use the Type E superheater. A pair of branching pipes for this type is shown in Fig. 16. The superheater flues are $3\frac{1}{2}$ inches in diameter, and the pipe goes down and back in one flue and repeats the journey in a second flue. After this double return trip through the pipe

surrounded by the hot flue gases, the steam is "superheated" and is ready for its work in the cylinder.

Superheated steam is steam at a temperature above that at which the water boiled to produce it. The temperature

FIG. 16.




at which water boils depends on the pressure. In Philadelphia, in an open saucepan, water boils at 212° F. A reduction in pressure lowers the boiling point. In Denver, a mile high, the pressure of the air is less by about 3 psi. and water boils at 202° F., which adds about half a minute to the time for a soft boiled egg.

An increase in pressure raises the boiling point. In a boiler with the safety valve set at 250 psi. the temperature at which the steam is produced will be 401° F. So long as the steam stays in the boiler in contact with water, it is "saturated" and the temperature remains the same no matter how vigorously the water boils. When the steam leaves the boiler and enters the hot superheater pipe, it is out of contact with the water and its temperature can be raised without changing the pressure. In American locomotive practice the steam reaches the cylinders at a temperature of about 700° to 750° F.

Speaking in round figures, the use of superheated steam increases by twenty to twenty-five per cent. the amount of power to be obtained from a locomotive of a given weight. This gain in power is based on better cylinder efficiency, which is due to two causes. In the first place superheating adds to the heat carried by a pound of steam and thus increases the amount of work that it can do. In the second place, when the steam is admitted to the cylinder which has been cooled during the preceding stroke, superheated steam holds on to

its heat better than saturated and there is less loss by useless transfer of heat to the cylinder walls.

The first high temperature locomotive superheater was applied by Dr. Wilhelm Schmidt on the Prussian State Railways in 1897. The first application outside of Germany was made by Mr. H. H. Vaughan on the Canadian Pacific Railway in 1901. Today no locomotive of any size is built without a superheater.

Steam pressure as well as steam temperature must be high if the best possible cylinder efficiency is wanted. Pressure is necessary to allow full expansion of the steam at full power.

On starting a locomotive steam is admitted to act on the piston with nearly full boiler pressure throughout most of the stroke. This is not economical, but can be tolerated at slow speed, when the horsepower is low.

As speed increases the dosage of steam per stroke is reduced. Steam is admitted to the cylinder during only a fraction of the stroke. Then the valves cut off the admission of further steam and the steam in the cylinder expands, turning heat into work by pushing the piston ahead. The steam in the cylinder loses temperature and pressure as it expands. In the steam locomotive the final pressure cannot be carried too low, as a pressure of 5 to 10 psi. is needed to get the steam out of the cylinders and produce the smokebox draft. To obtain a high ratio of expansion without dropping below this final pressure, the initital pressure must be high.

Table III shows how the thermal efficiency of the cylinders

TABLE III.

*Expansion and Efficiency of Steam Admitted at a Temperature of 650° F. and at Various Pressures and Expanded Adiabatically in the Locomotive Cycle to 35 Psi. Gage Release Pressure and Exhausted from this Volume against a Back Pressure of 10 Psi. Gage.*

| Admission Pressure Psi. Gage. | Number of Expansions. | Heat Units per Pound of Steam. | | Theoretical Thermal Efficiency Per Cent. | Lbs. of Steam per 1 H.P. per Hour. | Relative Efficiencies. | | |
|---|---|---|---|---|---|---|---|---|
| | | On Admission. | Utilized. | | | | | |
| 250 | 3.6 | 1344 | 204 | 15.1 | 12.5 | 100 | — | — |
| 335 | 4.6 | 1338 | 222 | 16.6 | 11.5 | 108 | 100 | — |
| 435 | 5.9 | 1332 | 238 | 17.9 | 10.7 | 117 | 109 | 100 |
| 585 | 7.8 | 1323 | 255 | 19.3 | 10.0 | 125 | 115 | 107 |

varies with the admission pressure (15). Calculation is based on the so-called locomotive cycle, with expansion to a pressure of 35 psi., release at this pressure, and exhaust against a back pressure of 10 psi. With an admission pressure of 250 psi., this gives 3.6 expansions and a theoretical efficiency of 15.1 per cent. By raising the admission pressure to 435 psi., the number of expansions can be increased to 5.9 with a theoretical efficiency of 17.9 per cent., a gain of about 17 per cent.

If steam is to be used successfully, the higher efficiencies of the higher steam pressures should be aimed at, and in this case careful consideration must be given to the cylinder design to allow for increased expansion under proper conditions.

With conventional cylinders and valve gear, it is hardly practicable to cut off admission at less than twenty-five per cent. of the stroke. This ratio of expansion can be increased somewhat by the use of special valve gears and poppet valves which make a cut-off of about 15 per cent. mechanically possible. Somewhere about this point, however, thermal conditions must be considered if the full value of the expansion is to be effective in increasing cylinder efficiency. As the steam expands, transforming its heat into work, its temperature falls. Therefore the steam when exhausted after expansion is much cooler than it was on admission. The metal of the cylinders follows this drop in temperature to a certain extent. That means that after expansion the cylinder is considerably cooler than the steam to be admitted for the next stroke. Consequently some of the heat in the incoming steam goes to warm the cylinder instead of doing work. The greater the expansion, the greater the temperature difference and the greater the loss from this cause which offsets a part of the gain due to a high expansion ratio. To reduce this loss, the expansion can be divided between two cylinders, as in the Norfolk and Western engine of an earlier slide.

This is the so-called "compound expansion" or "compounding." The steam after partial expansion with a low temperature range in the high pressure cylinders is transferred to a second larger pair of low pressure cylinders where expansion is completed. The total ratio of expansion is high, but the temperature range in each cylinder is moderate.

Compounding was extensively used thirty-five years ago

and proved conclusively that it gave better cylinder efficiency. Then, because of mechanical difficulties not directly affecting the double expansion, the use of compound cylinders declined in this country and disappeared except on the Norfolk and Western and on the Delaware and Hudson. The latter is an entirely isolated culture which has little effect on the practices of the other railroads.

If the steam locomotive is to compete with other forms of transportation, it must work with the highest possible efficiency, developing maximum power with minimum weight and fuel consumption. With this in view, it does not seem that American builders can afford to overlook what is being done with compound cylinders in France. Table II is recalled, and attention is directed to the last two lines. The Hudson type locomotive of line 4, which ranks among the best in this country, develops 25 horsepower per ton, while the Paris-Orléans engine does 25 per cent. better and develops 31 horsepower per ton. The American locomotive designer has evidently not achieved the ultimate. Progress has been made, but there is still room for further progress.

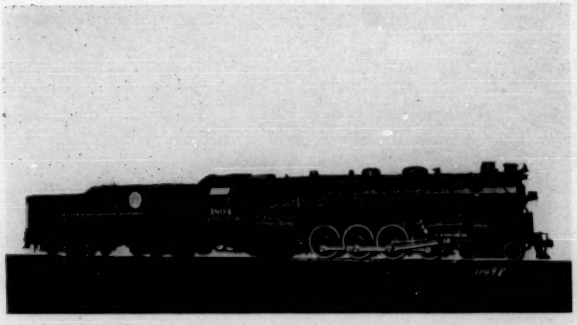
In closing I sum up the "conditions and relations" confronting the modern steam locomotive designer. The steam locomotive provides a mechanically desirable form of motive power. It can be purchased and maintained at a reasonable cost. There is, however, room for greater efficiency. To achieve this the boiler must be designed to give high combustion efficiency and reasonable efficiency of heat absorption. The cylinders must use a high ratio of expansion with high temperature steam.

In the synopsis on the admission cards, I promised a hesitant look ahead. I hesitate because thirty years ago I ventured the prophecy that the locomotive of the future would be a four-cylinder compound. Recently I was reminded of this, and my critic pointed out that today a great many locomotives are not four-cylindered, and still more are not compounded. Of course, my answer was that the locomotive of today is not yet the locomotive of the future. I hope that we may all be able to check up together on this matter in another thirty years. I think that we shall find the steam locomotive still at work with an increase in the

proportion of four-cylinder locomotives, and perhaps an increase in the number of compounds.

Now leaving the theoretical future for the practical present, I show some slides illustrating powerful locomotives which have been built in the last few years. We take first three freight locomotives. Fig. 17 is a 240-ton 4–8–4 type

FIG. 17.



locomotive. With eight driving and eight carrying wheels, it is adapted for fairly heavy trains at medium high speeds. Fig. 18 is a 320-ton 4–8–8–2 locomotive for the Southern Pacific. This is an exceptionally heavy machine with four cylinders and two engines articulated. It has an unusual arrangement by which the cab runs ahead. This relieves the enginemen from smoke and fumes in the numerous tunnels and snow sheds. Fig. 19 shows another locomotive for heavy drags on the difficult mountain grades of the West. This engine is for the Northern Pacific and with a weight of 361 tons is, I believe, the heaviest locomotive in the country.

Now we have a group of passenger locomotives which have been put into high speed service in the last few years. The locomotives pictured all carry some form of streamlining, but in several cases locomotives of the same class have been put into service without this modernistic touch. Without doubt, streamlining will reduce the air resistance of a locomotive at

FIG. 18.

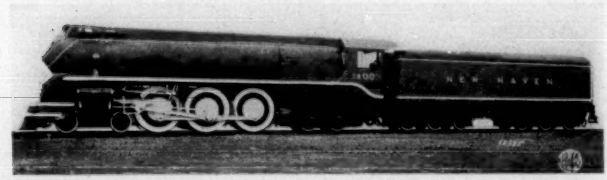
high speeds. It also improves the appearance of the locomotive. The actual earning capacity of streamlining seems, however, to be still an open question.

FIG. 19.

The Pennsylvania Railroad high speed electric locomotive, Fig. 10, may be compared with the high speed steamers. Streamlining in this case is necessarily limited to a rounding off of corners and a careful arrangement of the painted gold lines.

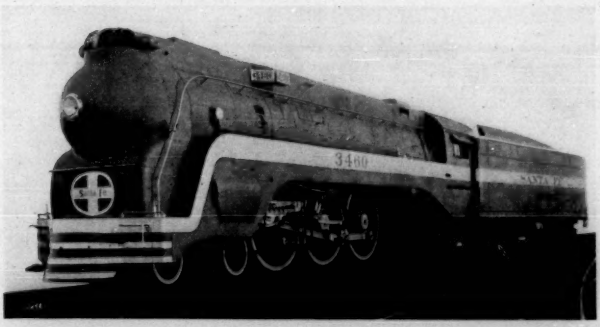
In all of the steam locomotives the stack, sand boxes, and domes on top of the boiler are smoothly shrouded. The New Haven, Fig. 20, provides a conical prow. The Santa Fe, Fig.

FIG. 20.




21, adds a shrouding for the cylinders. The Milwaukee, Fig. 22, uses the cylinder shrouding and gives the prow a smoother, though perhaps less attractive appearance. This is a really high speed locomotive; recently one of this type took the

FIG. 21.

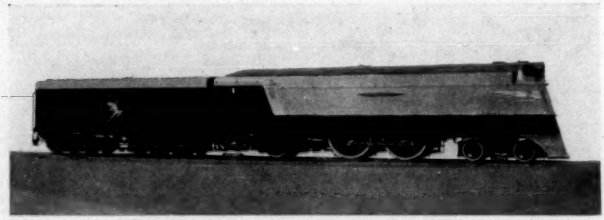



"Hiawatha" train 20 miles at a speed of over 100 miles per hour, and for five miles the speed indicator hand was trying to get past the maximum figure of 120 miles per hour.

Fig. 23 shows the London, Midland and Scottish "Royal Scot" locomotive. Its weight of 120 tons is less than two-

thirds that of its American contemporaries. Compared with the American locomotives the streamlining of the "Scot" looks as though it had been designed more to reduce air resistance and less to improve appearance.

FIG. 22.



The clock reminds me that a speaker, like a locomotive, must have terminal facilities. In tonight's paper I have directed attention to first principles and have made no attempt to deal with the very large number of appliances offered to

FIG. 23.

improve the efficiency of the steam locomotive. Their name is legion, and many play important parts.

The final picture, Fig. 24, from a photograph by my friend, Mr. Paul Warner, shows some of the glamor of the steam locomotive. Titling it, "Steaming Ahead," I hope that it may be typical of the future for the locomotive and for all of us.

Before stepping down, I want to thank all of my friends and others to whom I am indebted for material for tonight. They are so numerous that I cannot name them in detail.

FIG. 24.

I, therefore, take for my epilogue Kipling's prologue to "Soldiers Three":

"When 'Omer smote 'is blooming lyre
'E'd 'eard men sing by land and sea,
And what 'e though 'e might require
'E went and took, the same as me."

BIBLIOGRAPHY.

1. History of the First Locomotive in America, by Wm. H. Brown, 1871.
2. John Stevens, by A. D. Turnbull, 1928.
3. Locomotive Power Development on the Pennsylvania Railroad System 1831–1924, by Paul T. Warner, 1924.
4. Illustrated Catalogue of Locomotives, Burnham Parry Williams & Co., 1881
5. Railway Location, by A. M. Wellington, 1908.
6. Centenary History of the Liverpool and Manchester Railway, by C. F. Dendy Marshall, 1930.
7. A Century of Locomotive Building, by J. G. F. Warren, 1923.
8. *Journal of Institution of Mechanical Engineers*, June, 1939.
9. A Study of the Locomotive Boiler, by Lawford H. Fry, 1924.
10. A Practical Treatise on Locomotive Engines, by Comte F. M. G. de Pambour, 1840.
11. Heat Balances for Locomotive Boilers, by Lawford H. Fry, *Engineering*, June 17, 1938.
12. Combustion and Heat Balances in Locomotive Boilers, by Lawford H. Fry, *Inst. Mech. Engrs.*, 1908.
13. Transfer of Heat between a Flowing Gas and a Containing Flue, by Lawford H. Fry, *Trans. A. S. M. E.*, 1917.
14. Heat Transfer in the Locomotive Superheater, by Lawford H. Fry, *Trans. A. S. M. E.*, 1929.
15. High Pressure Steam in Locomotive Cylinders, by Lawford H. Fry, *Trans. A. S. M. E.*, 1927.

**Dry Ice Used to Increasing Extent for Perishable Shipments.**—C. T. LONGAKER. (*Railway Age*, Vol. 109, No. 5.) The carbon dioxide industry has been working for a number of years to popularize the use of dry ice, for refrigerating perishable commodities shipped by rail, but made little real progress until comparatively recently when it was shown that no specialized equipment need be installed at additional cost in the refrigerator cars. With this limitation removed and a considerable background of satisfactory service performance, dry ice is now being used to an increased extent for railroad perishable shipments. The recently simplified method of applying dry ice to refrigerator-car shipments is to use a combination of wet and dry ice in the regular bunkers of standard refrigerator cars without the employment of any special equipment. The refrigerating effectiveness and the economic value of this method have been demonstrated in a series of operating tests conducted by research engineers of the Liquid Carbonic Corporation in collaboration with several railway refrigerator-car lines. These tests have shown, among other things, that the use of dry ice in combination with water ice in standard refrigerator cars with 2½ in. of insulation thickness, furnishes the same service as water ice in super-insulated cars that have 5½ in. of insulation. It is not necessary for the carriers to rush into competitive building programs to furnish shippers super-insulated cars since water ice and dry ice will get the same results. One of the tests made to determine comparative results of the use of water ice in a super-insulated car versus the use of water-ice-dry-ice combination in a standard car was completed on a shipment from Indianapolis, Ind., to San Francisco, Cal. The type of lading and outside temperatures were practically the same in both cases. Comparative ice consumptions and costs are shown as a reduction in total expense from $31.40 to $27.39 in favor of the wet and dry-ice combination.

R. H. O.

# REPORT OF COSMIC RAY OBSERVATIONS MADE ON THE U. S. ANTARCTIC EXPEDITION IN COÖPERATION WITH THE BARTOL RESEARCH FOUNDATION.

BY

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AND

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## INTRODUCTION.

BARTOL RESEARCH FOUNDATION
Communication No. 102.

In accordance with the broad purposes of the United States Antarctic Expedition, to provide results of scientific value in as many fields as possible, a program of cosmic ray observations was included in the agenda of the expedition. One of us (S. A. K.) was invited to formulate a series of cosmic ray observations which might be undertaken by the expedition. This program was designed with certain limitations in mind, and was intended to yield such new information as might be obtained by cosmic ray observations in the region near the South magnetic pole with simple and reliable equipment. It was not possible to include any observation which called for elaborate equipment or which required the use of much power. The program which is described below was drawn up and approved, the apparatus was assembled, and when the expedition sailed on November 21, 1939, one of us (E. T. C.) accompanied it to carry out the first part of this plan.

The apparatus was carried on board the USS North Star, supply ship of the expedition. The ship went from Philadelphia, U. S. A., via the Panama Canal, Pitcairn Island, Wellington and Dunedin, New Zealand, to Little America (latitude 79° South, longitude 164° West, geomagnetic latitude 77° South). Thence it sailed to Valparaiso, Chile, and to East Base in Palmer Land (latitude 68° South, longitude 67° West, geomagnetic latitude 57° South). From East Base the

ship returned via Valparaiso to Panama. The route of the ship is shown in Fig. 1. A preliminary report of some of the results has been presented by the authors.[1]

PROGRAM OF COSMIC RAY OBSERVATIONS.

(*A*) *Latitude Effect Observations.*—Two of the three cosmic ray meters available for this expedition, namely one of the two Millikan type electroscopes loaned by the Carnegie Institution of Washington and a Geiger counter apparatus built at the Bartol Foundation, were operated on board ship between Philadelphia and Little America. Three problems presented themselves in this connection. These problems were: (*a*) does the variation of intensity with latitude shown by the counter agree with that shown by the electroscope? (*b*) what is the variation of intensity with latitude south of New Zealand? (*c*) will the intensity be symmetrical at corresponding North and South latitudes? (*d*) can correlations with external temperature be found with these instruments and in these latitudes, as was found by Compton [2] in the north?

(*B*) It was also planned to make airplane flights with one of the Millikan meters to as high elevations as possible, and to analyze the record of the variation of intensity with altitude for any asymmetry between far North and far South intensities. This program called for (*a*) flying the meter at several elevations for as long as practicable, and (*b*) making corrections for local and airplane radioactivity.

(*C*) It was planned to make a long-period installation of the two Millikan cosmic ray meters to operate over the current winter. These records will be analyzed next year, when they can be obtained from the Antarctic, for correlations between fluctuations in the cosmic ray intensity and various terrestrial phenomena, including magnetic storms, aurorae, and external temperature. Bursts in the ionization are being recorded.

(*D*) A Geiger counter apparatus, designed to measure the total cosmic ray intensity from all directions, was operated on the ship both between Philadelphia and Little America and on the continuation of this voyage, back to Valparaiso, down to Palmer Land and then back to the Canal Zone, thus providing

[1] E. T. Clarke and S. A. Korff, *Phys. Rev.*, **58**, 180 (1940).

[2] A. H. Compton and R. N. Turner, *Phys. Rev.*, **52**, 799 (1937).

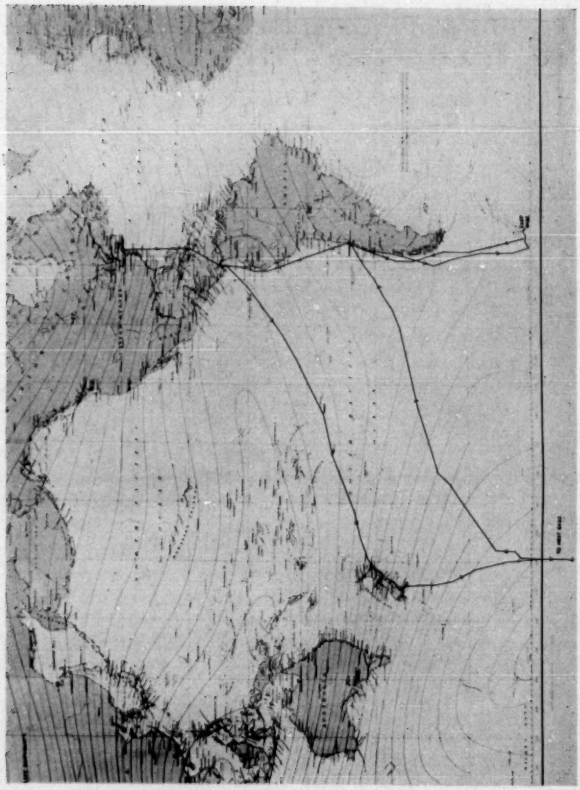


FIG. 1.

Route of the USS North Star, on map showing lines of equal horizontal magnetic intensity.

four runs over the essentially new part of the latitude-variation curve, namely that south of geomagnetic latitude 40° South.

(*E*) Data on meteorology and associated phenomena were kept. These were essentially (*a*) for direct use with the records obtained, and (*b*) to permit evaluation of the possibilities for further work at the stations.

### THE PRESENT STATE OF THIS WORK.

Section *A*, concerning latitude effect, has been carried out, and the report will be found below. With regard to section *B*, several airplane flights have been made, one to an elevation of 21,000 feet, with one of the electroscopes. The records of these flights were not obtained in time to come out with the supply ship and consequently will not be available until next year. Under section *C*, the installations have been effected and the meters are now in operation. Reports will again not be available until next year. The apparatus referred to in section *D*, and the meteorology notes in section *E*, are discussed below.

### LATITUDE EFFECT OBSERVATIONS.

#### 1. Counter Apparatus.

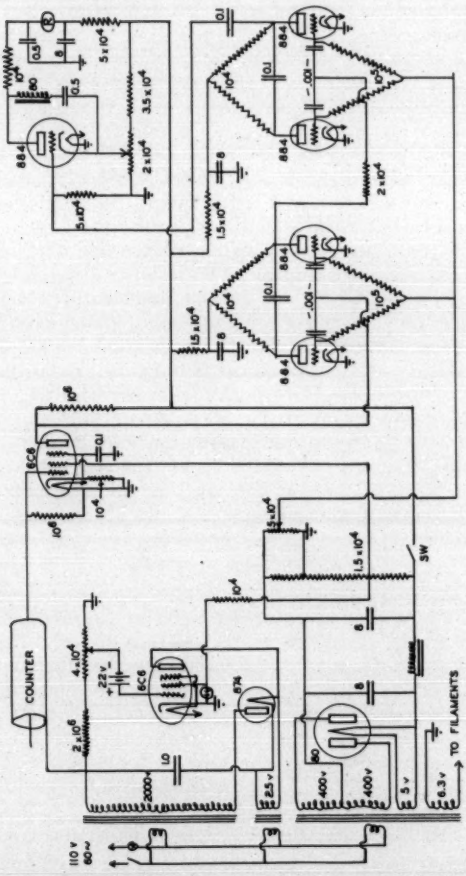
The instrument used for measuring the total cosmic ray intensity from all directions consisted of a single Geiger counter, the cylinder of which was 23 cm. long, 5.8 cm. in diameter, filled with 6 cm. argon plus 1 cm. ethyl alcohol. This counter has a "plateau" about 450 volts wide and was operated in the middle of this range at about 1250 volts. The counter was mounted inside a lead shield 7.5 cm. thick. The impulses from the counter were scaled down 4 : 1 using a thyratron scaling circuit of the type described by Wynn-Williams,[3] and the scaled counts were recorded on a watch recorder. With this arrangement approximately 190,000 total counts per day were recorded. Fig. 2 shows the circuit used.

The high potential for the counter was supplied by a modified Street-Johnson[4] voltage regulating circuit which

[3] C. E. Wynn-Williams, *Proc. Roy. Soc. A*, **136**, 312 (1932).

[4] J. C. Street and T. H. Johnson, J. FRANK. INST., **214**, 155 (1932).

FIG. 2.




Circuit of counter Control and recording set. Resistances in ohms, capacities in microfarads. Elements of this circuit are power supply, voltage stabilizer, counter amplifier, and scale-of-four with thyratron recorder.

kept this voltage fixed. Fluctuations as large as ± 20 volts in the 110-volt primary line were found to have no effect on this counter voltage.

Tests showed the desirability of providing accurate control of the grid bias voltage in the scaling circuit, so that the thyratron grids could be set to operate in the middle of their stable operating voltage range. When the grid potentials were thus adjusted, a change in the primary voltage of ± 15 volts was found to make no difference in the recorded counting rate. Greater changes did introduce a difference, since the grid bias of the thyratrons, which was obtained from a bleeder across the plate voltage supply, then assumed a value which resulted in unstable operation. Tests also showed that temperature changes of 20° C. in the temperature of the box containing the voltage supply and scaling and recording unit introduced no observable change in the counting rate.

Preliminary tests have shown a temperature coefficient of the counter itself of − 0.15 per cent. in the counting rate per degree C. temperature rise. This effect is being studied further. During the course of the observations made with it on the expedition, however, the apparatus was run in a cabin where the temperature was kept approximately constant, and so this effect did not become serious.

### 2. Geiger Counter Observations.

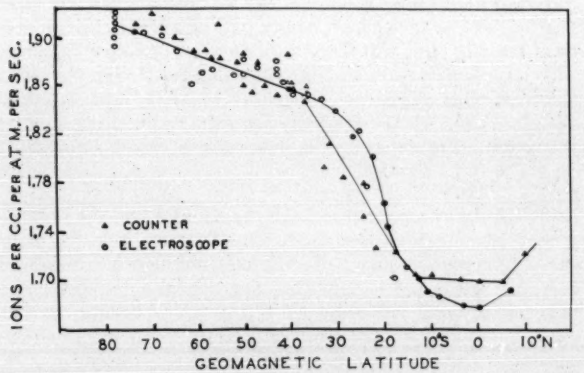
The observed daily mean counting rates were corrected for changes in barometric pressure by using an assumed barometer coefficient [5] of − 0.17 per cent.* per millimeter Hg. The corrected counting rates, after having been multiplied by an arbitrary constant to enable them to be shown on the same scale as the electroscope ionization, were plotted against geomagnetic latitude, and are presented in Fig. 3. The accuracy of each point, on the basis of the number of counts per day, is ± 0.3 per cent.; the distribution of the various daily

[5] R. L. Doan, *Phys. Rev.*, **49**, 107 (1936).

* This figure was found to be consistent with a coefficient calculated from the data obtained when the meter was not changed in latitude, i.e., when the ship was in port. These runs in port were not long enough to permit any great accuracy; on the other hand, admissible changes in the barometer coefficient would not substantially alter the results presented.

means, however, suggests that the normal fluctuations of the cosmic ray intensity at any latitude are ± 0.7 per cent. The observations show a definite "knee" in the cosmic ray intensity curve at about geomagnetic latitude 39° South. Between this latitude and the equator a drop of 8 per cent. occurs, while between 39° and 77° South, a variation of 3 ± 0.3 per cent. is found.

FIG. 3.




Cosmic ray intensities as measured by electroscope and counter, in Southern latitudes. The differences between curves in middle latitudes is due to longitude effect. Each point is a daily mean. The electroscope remained on board ship at 77° South for six days before being put ashore, and the normal daily fluctuations may be judged from the corresponding six points. The data are not corrected for external temperature.

### 3. Electroscope Observations.

An electroscope of the type described by Millikan and Neher [6] was operated on board the ship on the run from Philadelphia via Panama and Dunedin, N. Z., to Little America. This instrument was mounted inside a 10 cm. thick lead shield, the lead being held in an iron case 1.25 cm. thick, making an equivalent shield of 11 cm. lead.

The ionization measured in this instrument, when corrected for barometric variations using a barometer coefficient of − 0.17 per cent. per millimeter Hg, and the ionization due to bursts having been subtracted, is presented in Fig. 3. In

[6] R. A. Millikan and H. V. Neher, *Phys. Rev.*, **50**, 15 (1936).

this curve, the daily means of ionization produced by cosmic rays are plotted against geomagnetic latitude.

In comparing this curve with that of the counter, it must be remembered that the points between 0° and about 40° south latitude were obtained at different longitudes. The electroscope was run between Philadelphia and Little America, while the Geiger counter apparatus, which was completed just before the ship sailed, was not put into proper operating order until after Dunedin, N. Z. On the part between geomagnetic latitude 40° South and 77° South, the two curves are strictly comparable. In Fig. 1 it will be seen that the course taken by the electroscope (through Pitcairn Island and New Zealand) lies in regions of greater horizontal magnetic intensity, and therefore lower total cosmic ray intensity, than that taken by the counter apparatus, up the west coast of South America.

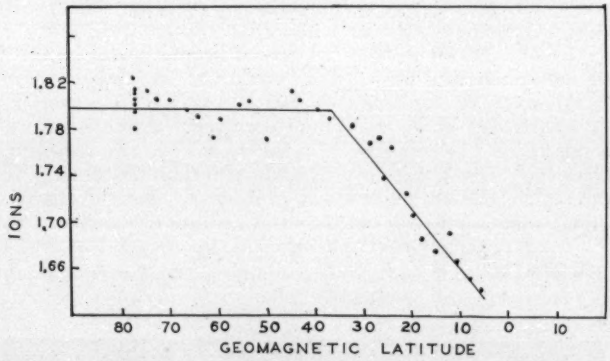
### DISCUSSION OF THE LATITUDE EFFECT OBSERVATIONS.

It will be observed that both the counter and the electroscope measurements show the familiar "knee" in the intensity curve at about geomagnetic latitude 39° South. South of here, the intensity is found to rise slightly, the total rise between 39° and 77° being $\Delta I = 3 \pm 0.3$ per cent. It was found that the application of an external temperature coefficient of $-0.15$ per cent. per degree C. caused the curve to be horizontal south of 39°. This value may be considered to be in substantial agreement with the coefficients determined in other regions by the observers cited below. The observations thus corrected are shown in Fig. 4. This coefficient, $\Delta I/\Delta T$, was determined by considering the change in intensity observed and the average external temperature change $\Delta T$ of 20° C. It has not yet been possible to determine the coefficient by correlating the intensity with the temperature at one location since the various meters did not, on this trip, remain in one place for any sufficient time. It is hoped that a good determination may be obtained from the meters now installed at Little America. Further, it will be recalled that Compton and Turner [2] have found an external temperature coefficient of $-0.18$ per cent. per degree C. applicable in the Northern hemisphere as a yearly average, and that Gast and Loughridge [7]

[7] P. F. Gast and D. H. Loughridge, *Phys. Rev.*, **58**, 194 (1940).

find — 0.11 per cent. per degree C. As Hess [8] has pointed out, there appears to be a seasonal variation in the external temperature coefficient, a minimum value being found in the warm months. Hence the coefficient adopted appears to be entirely reasonable, and may be expected to be larger during the cold months.

FIG. 4.




Electroscope ionization curve corrected for external temperature effect by coefficient of — 0.15 per cent. per degree C.

**BURSTS.**

A total of 154 bursts were recorded by the Millikan-Neher meter during 43 days of operation. These were classified according to size, and are presented in Table 1.

TABLE 1.

| Energy of Burst Ion-pairs × $10^6$. | Number Observed. | Energy of Burst Ion-pairs × $10^6$. | Number Observed. |
|---|---|---|---|
| 2.2– 4.3 | 74 | 11.8–13.3 | 1 |
| 4.3– 5.8 | 43 | 13.3–14.8 | 0 |
| 5.8– 7.3 | 14 | 14.8–16.2 | 1 |
| 7.3– 8.8 | 9 | 16.2–30.2 | 4 |
| 8.8–10.3 | 2 | 30.2–45.2 | 2 |
| 10.3–11.8 | 3 | 45.2–90 | 1 |

Summary of all bursts observed, classified to show distribution-in-energy.

[8] V. F. Hess, *Phys. Rev.*, **57**, 781 (1940).

It will be recalled [9] that the number of bursts $R$, as a function of their energy $N$ (defined as the number of ion-pairs produced in the burst), may be expressed by

$$R = AN^{-s}, \tag{1}$$

where $A$ is a constant, and $s$ is a number which is adjusted to give the best fit to the observational data. In this table, $s$ is found to be $3.0 \pm 0.3$, a value in good agreement with that previously reported by one of us.[10]

It was also found that the rate of occurrence of bursts in the instrument, while the ship was north or south of 20° North or South geomagnetic latitude respectively, was $2.7 \pm 0.2$ per day, while the rate of occurrence in the equatorial zone, namely between 20° North and South, was $2.5 \pm 0.3$ per day. This suggests a latitude effect in the bursts [11] of the same order as that in the total intensity, but the observational uncertainty will not permit a definite evaluation.

The largest burst recorded during the voyage (see Fig. 5) was one of $N = 83.6 \times 10^6$ ion-pairs, or represented the

FIG. 5.

Largest burst recorded during the voyage. The abrupt vertical displacement of the diagonal line traced by the electroscope needle indicates the sudden formation of $83.6 \times 10^6$ ion-pairs in the instrument.

liberation of $2.7 \times 10^9$ e-v as ionization in the chamber. Since

$$N = MLPI \tag{2}$$

where $L$, the average path length of a ray passing through the electroscope, is 10 cm., and the instrument contains $P = 30$ atm. of argon, if we suppose that the specific ionization $I$ of

[9] C. G. Montgomery and D. D. Montgomery, *Phys. Rev.*, **48**, 969 (1935).
[10] S. A. Korff, J. Terr. Mag., **43**, 227 (1938).
[11] W. P. Jesse and P. S. Gill, *Phys. Rev.*, **55**, 414 (1939).

each ray per cm. per atm. is 50 ion-pairs, then this represents the passage of $M = 5600$ simultaneous rays through the instrument. If we suppose that the burst was accompanied by the production of nuclear particles, then it would require 150 protons ending their ranges [12] on average paths through the chamber to produce this amount of ionization.

### SPECIFIC IONIZATION.

Since the counter measures the number $m$ of particles passing through it, per cm.$^2$ per second, regardless of the energy of each particle, while the electroscope measures the integrated total of the ionization formed along the tracks of all the particles passing through it, the comparison of these two data [13] will yield the average amount of ionization $N$ per cm. path of the particles in the gas of the electroscope. For the case of radiation incident on a sphere, the relation between these quantities is

$$i = mNAL/V \qquad (3)$$

where $L$ is the average path length of particles through the electroscope, $i$ is the observed electroscope ionization, in this case 1.63 ions per cc. per atm. of standard air per second (inside lead), $m$ is the flux of cosmic rays crossing each horizontal sq. cm. per second, $A$ is the cross-sectional area of the electroscope, and $V$ its volume. For a sphere, $AL/V$ is unity. $m$ is obtained from the counting rate of the counter by dividing the total counting rate by the effective area and multiplying by the counter efficiency. In this case $m$ (inside lead) was found to be $2.1 \pm .1 \times 10^{-2}$ cosmic ray particles crossing unit horizontal area per second from all directions, and hence we find $N$ (also inside lead) to be about 77 ion-pairs per cm. per atm. This figure may be compared with 68 found by Brode [14] (in air) by counting droplets in a cloud chamber. It will be observed that the radiation is somewhat more ionizing, on the average, than is to be expected from the specific ionization produced along the tracks of single rays.

It should be noted that the figure for the average specific ionization found in cloud chambers is quite close to the

[12] R. M. Livingston and H. A. Bethe, *Revs. Mod. Phys.*, **9**, 268 (1937).
[13] S. A. Korff and W. E. Danforth, J. FRANK. INST., **228**, 159 (1939).
[14] R. B. Brode, *Revs. Mod. Phys.*, **11**, 222 (1939).

minimum value from the curve of ionization as a function of energy. A change in the average energy distribution will alter this figure upward.

In this discussion we refer to measurements made inside an 11 cm. thick lead shield. Therefore we may consider that none of the electrons generated in the air above the instruments by the radiation will penetrate the measuring chambers. Furthermore, since these observations were made at sea level, or 10 meters of water equivalent below the top of the atmosphere, practically all primary electrons will also have been eliminated. We are therefore in the following section discussing mesotrons and secondaries produced by these in the lead shielding.

If we suppose that the additional ionization exhibited by the average particles is due to electron secondaries generated mostly in the lead shield and walls of the instrument, then the ratio of the ionization $N$ per cm. path found from the electroscope-counter comparison to the ionization $Q$ found along the tracks of single rays, will be

$$N/Q = (m + s)/m, \tag{4}$$

where $m$ is the number of mesotrons passing through unit area per unit time, and $s$ is the number of secondaries accompanying each mesotron through the apparatus. If we take $N/Q$ as 1.14 from the data, then $s/m$ is 0.14. This figure represents the average number of secondaries accompanying each mesotron below the lead shield. This value should not be regarded as being established to better than about 50 per cent., for admissible changes in the value of $m$ will change this considerably. According to Bhabha's [15] theory of production of knock-on electrons by mesotrons, the average number of electrons accompanying a mesotron below 11 cm. of lead will be 0.08, a figure with which the above is, while somewhat larger, in sufficient agreement.

Further, the specific ionization (under 11 cm. of lead) does not vary with latitude. A change in $N$ of 0.5 per cent. would have produced an observable divergence between the counter and electroscope readings between 40° and 77° South geomagnetic latitude. Hence we conclude that the

[15] H. J. Bhabha, *Proc. Roy. Soc. A*, **164**, 257 (1938).

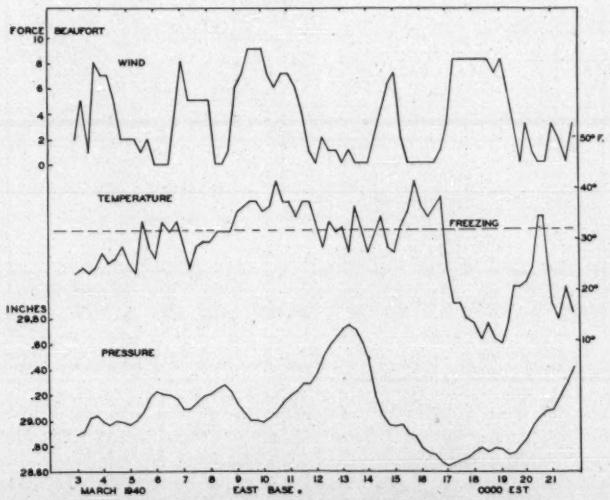
ratio of electrons to mesotrons is constant at all latitudes south of the knee. This conclusion is to be expected, since practically no electrons can enter the measuring chamber through the 11 cm. lead shield, and justifies our earlier assumption that inside the measuring chamber all electrons are secondary to the mesotrons.

Since the number of mesotrons south of the knee is constant with increase in latitude, while the lower limiting energy of the primary particles decreases, the mesotrons which reach sea level must have all been produced by primaries whose energies are equal to or greater than the cut-off energy at the knee.

## NOTES REGARDING METEOROLOGY.

The pressure, temperature, and wind observations at East Base for three weeks during the summer, March 3–21, 1940, are presented in Fig. 6. It will be observed that the pressure

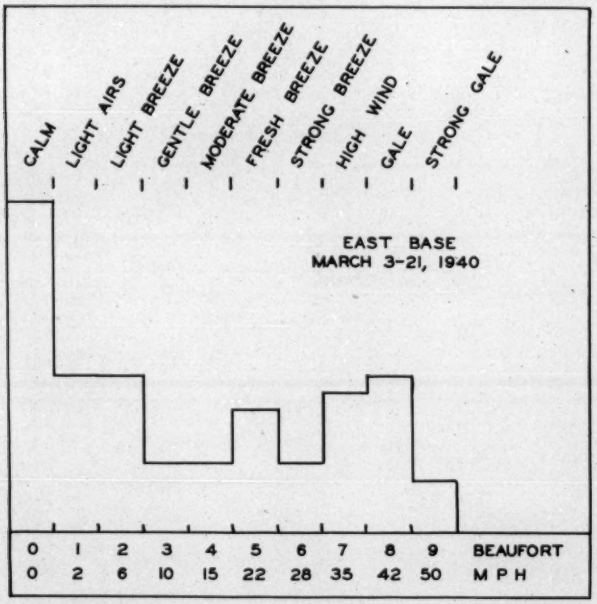
FIG. 6.




Wind, temperature, and pressure recorded at East Base (Palmer Land) during the three weeks stay of the North Star. Note large variability in the wind velocities. Diurnal effects in temperatures are evident, but are not seen in the pressure curve.

averages around 29 inches, considerably below that in the temperate zones. Large pressure changes occur, but the diurnal variation is small. The temperature only once went far below freezing, and showed a diurnal variation of about 10° F. The wind velocity distribution (see Fig. 7) is very

FIG. 7.




Wind distribution at East Base during March 1940. Abundant strong winds will be noted, although winds are of force 0 to 2 for fifty per cent. of the time. In temperate latitudes much fewer winds above force 4 are encountered.

different from that in temperate latitudes, with winds of gale force occurring about fifteen per cent. of the time. On the other hand, about fifty per cent. of the time the air was calm or at the most a light breeze. Consequently the base is entirely suited for balloon work, if proper moments are chosen.

The meteorology at West Base (Little America) is sufficiently similar not to justify presenting the data. The temperatures seldom went far below freezing between January 12–24, 1940, the average being about 20° F. The pressure averaged around 29.2 inches. Winds have a more normal distribution, with fewer gales and, again, many calm periods.

ACKNOWLEDGMENTS.

We wish to acknowledge assistance received from various sources, especially from the Carnegie Institution of Washington. We are indebted to J. A. Fleming for helpful support, to F. Alton Wade for assisting with cosmic ray observations, and to our colleagues at the Bartol for stimulating discussions. We also wish to acknowledge the courtesy of the Eastman Kodak Company for supplying the recording film for the cosmic ray electroscopes, and to the Burgess Battery Company for making available batteries for operating the electroscopes.

**Survey of Rubber Producing Possibilities in Tropical American Countries.**—Survey of the tropical Americas to determine the most promising rubber producing areas in the western hemisphere has begun, Secretary of Agriculture, Henry A. Wallace, stated recently. Two exploration parties already are at work. Research along this line has been authorized by Congress with an appropriation of $500,000. The Latin American republics involved are coöperating. One party is at work in southeastern Central America and parts of Colombia, headed by O. D. Hargis, a rubber specialist. Another party is covering northwestern Central America as far north as Vera Cruz, Mexico. This is headed by Dr. Mark Baldwin, soils man from the bureau of Plant Industry. A third party, led by Dr E. C. Stakman, pathologist, is on its way to survey an area which covers roughly the headwaters of the Amazon tributaries—an area east of the Andes Eventually the surveys will take in an area extending from Vera Cruz to Rio de Janeiro on the southern edge of the Atlantic rain belt Observations made in these surveys, together with the department's already extensive knowledge of rubber growing in this hemisphere, will serve as a basis for determining, in coöperation with the countries involved, the locations of at least two experimental bases to be established in the most promising areas. Results of the rubber survey and experimental work that follows will be available to any American republic, and to both large and small growers. Rubber is a crop that may be produced profitably by either large or small growers if conditions of soil, climate and labor are right, and, if high yielding, disease-free trees are planted. The rubber tree, *Havea Brasiliensis*, may be grown in any warm climate with a rainfall of at least 70 inches, well distributed through the year It thrives in a wide range of soils and after it has reached an age of 7 to 10 years may be tapped every few days for years without apparent damage to the tree.

R. H. O.

V. 19

# PROPOSED STANDARD SOLAR-RADIATION CURVES FOR ENGINEERING USE.

BY

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Questions regarding sunlight are constantly occurring in illuminating engineering: How does illumination vary with the season and with the time of day? How much solar radiant energy will be absorbed by a given material to be used in the tropics? How effective are various infrared-absorbing glasses? What is the relation between altitude and amount of ultra-violet radiation? How does the color of sunlight vary with latitude? A great number of data have been collected on such subjects, but little attempt seems to have been made to compare these data, to correlate them, and to put them in a convenient form for engineering use.

In this paper a comparison is made of data obtained by various investigators on the spectral distribution of sunlight outside the earth's atmosphere. On the basis of this comparison, a *proposed standard curve*, expressed in absolute units, is recommended for use in engineering computations dealing with sunlight. Data for atmospheric transmission are given also, so that the resulting spectral irradiation curve can be computed for any part of the earth's surface at any time and for any elevation above sea level.

Since a large proportion of the world's population lives not far above sea level, an elevation near zero is the most generally useful one. Accordingly a set of *proposed standard curves* for the spectral distribution of direct sunlight has been computed for sea level. With such curves available, it is a simple matter to compute the illumination, the heating effect, the color, etc. A number of such calculations are carried through to check the proposed standard curves against data obtained in quite different ways. These checks indicate that the method yields results of sufficient accuracy for engineering use.

## 2. THE SOLAR CONSTANT.

The radiant energy at normal incidence, received at the surface of the earth from the sun, is subject to wide variations because of the following factors:

1. Variations in the sun itself.
2. Variations in the distance from earth to sun.
3. Differences in atmospheric scattering
   - *a*. By air molecules
   - *b*. By water vapor
   - *c*. By dust
4. Differences in atmospheric absorption by $O_2$, $O_3$, $H_2O$, $CO_2$, etc.

In 1881, Langley applied his newly developed bolometer to the measurement of spectral irradiation from the sun.[1] Measurements made with the sun at various zenith angles allowed him to compensate for the effect of the atmosphere and thus to calculate the solar irradiation,[2] at normal incidence, outside the atmosphere at the mean solar distance. This quantity is called the *solar constant*. Since 1902 the Smithsonian Institution has been engaged in a painstaking study of the solar constant and has collected evidence [3] that this quantity actually varies with time, the maximum fluctuations being approximately $\pm$ 1.5 per cent. The mean value of the Smithsonian results [3] from 1920 to 1934 is 1.9408 cal. cm.$^{-2}$ min.$^{-1}$. However, this value is on the basis of the 1913 Smithsonian standard,[4] which is now believed to be 2.3 per cent. high.[5] Thus the best value for the mean solar constant appears to be

$$1.9408 \times 0.977 = 1.896 \text{ cal. cm.}^{-2} \text{ min.}^{-1}.$$

On the basis of 4.1835 joules = 1 gram-calorie, the solar

[1] S. P. Langley, "The Bolometer and Radiant Energy," Am. Acad., *Proc.*, **8**, 1881, p. 342.

[2] The nomenclature used in this paper is in accordance with Moon, "Scientific Basis of Illuminating Engineering," New York, 1936, p. 560.

[3] C. G. Abbot, "Solar Radiation and Weather Studies," Smithsonian Misc. Coll., **94**, No. 10, 1935, p. 12.

[4] Smithsonian Institution, *Annals of Astrop. Obs.*, **3**, 1913, p. 134.

[5] Abbot and Aldrich, "The Scale of Solar Radiation," Smithsonian Misc. Coll., **92**, No. 13, 1934.

constant is therefore

**1322 watt m.$^{-2}$.**

This value is in good agreement with independent determinations.[6]

The actual irradiation at normal incidence may differ from the foregoing value, not only because of the effect of the atmosphere and because of fluctuations in the sun itself, but also because of variations in solar distance. This factor produces a maximum change in irradiation of approximately $\pm$ 3.5 per cent., the exact amount at any time of year being determined by well-known methods which need not be considered here.

### 3. SPECTRAL IRRADIATION CURVE.

As the next step, consider the curve of spectral irradiation outside the atmosphere. By far the greatest amount of information on this subject has been obtained by the Smithsonian Institution,[8] and some of their results are plotted in Fig. 1. Data obtained at Potsdam by Wilsing [7] are also included, as are the results of Pettit [9] and of Fabry and Buisson.[10]

The data of Fig. 1 are in arbitrary units, and thus it is permissible to move any set of data up and down on the diagram. The Smithsonian results were plotted directly from the table given by Abbot, Fowle and Aldrich,[8] while the other sets of points were shifted vertically to give the best match. The blackbody curve [11] was adjusted so that its

[6] See, for instance, C. Tingwaldt, "Ein neues Pyrheliometer für Absolutmessungen," *Zs. f. Instrumentenkde.*, **51**, 1931, p. 593. A. Unsöld, "Physik der Sternatmosphären," Berlin, 1938, p. 27.

[7] I. Wilsing, "Über die Helligkeitsverteilung im Sonnenspektrum nach bolometrischen Messungen," Astrop. Obs. Potsdam, *Publikationen*, **32**, No. 72, 1917, pp. 91, 92.

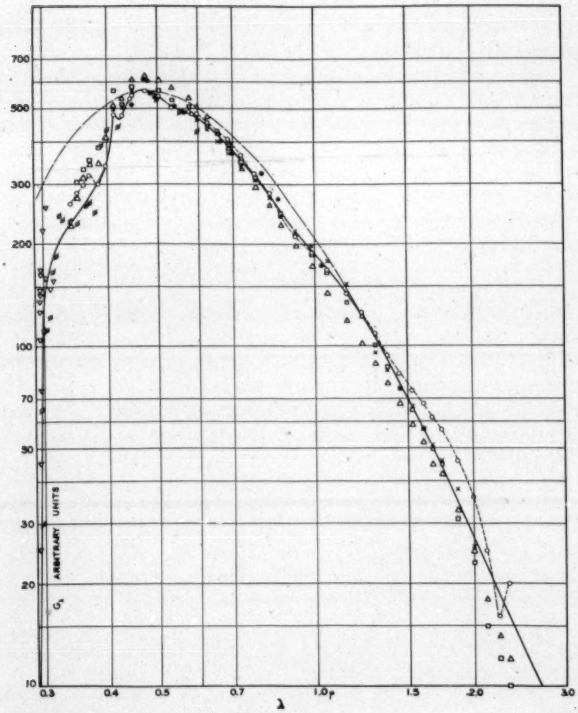
[8] Abbot, Fowle, and Aldrich, "The Distribution of Energy in the Spectra of the Sun and Stars," Smithsonian Misc. Coll., **74**, No. 7, 1923, p. 15.

[9] E. Pettit, "Measurements of Ultraviolet Solar Radiation," *Astrop. J.*, **75**, 1932, p. 185.

[10] Fabry and Buisson, "A Study of the Ultraviolet End of the Solar Spectrum," *Astrop. J.*, **54**, 1921, p. 297.

[11] P. Moon, "Tables of Planck's Function from 3500 to 8000° K.," *J. Math. and Phys.*, **16**, 1937, p. 133.

FIG. 1.




Solar irradiation on a surface outside the atmosphere.

▽ Fabry & Buisson
✱ Pettit
● Wilsing
△ 1903–1910
× 1903–1910 (omitting quartz results) } Smithsonian Institution
□ 1916–1918
○ – – ○ 1920–1922
— — Blackbody, 6000° K.
——— Proposed standard curve

maximum was approximately equal to the maximum of the 1920–22 curve.

The best result of the Smithsonian Institution is usually believed to be [8] the weighted mean of the 1920 and 1922 results, which is shown by the circles and the dotted curve of Fig. 1. In common with all other data, this curve indicates a narrow peak at 0.48 $\mu$ and a depression at 0.55 $\mu$. However, in the region from 0.60 to 0.75 $\mu$, the curve is higher than any of the other data, while in the region 0.85 to 1.0 $\mu$ it sinks below most of the other data. Thus there seems to be a question as to whether the 1920–22 representation is the best one in these regions. In an attempt to get the smoothest curve that is in agreement with the available information, I have used the 1920–22 results from 0.40 to 0.55 $\mu$ but have departed slightly from the Smithsonian results at longer wave-lengths, as indicated by the heavy curve of Fig. 1. At wave-lengths shorter than 0.40 $\mu$, there is reason to believe that the Smithsonian results are high because of scattered light in the monochromator. I have therefore favored the Pettit values between 0.32 and 0.40 $\mu$ and have used the Pettit and the Fabry-Buisson values at still shorter wave-lengths. In both of these investigations stray light was eliminated.

All the data indicate that the broad peak associated with the blackbody curve is not obtained in the solar spectrum. The depression of the solar curve from 0.50 to 1.0 $\mu$ appears to be so well substantiated that there would be no justification in substituting the Plankian curve in this region. At longer wave-lengths, however, the blackbody curve is actually a much better approximation to all the data than is the 1920–22 curve. Thus I have employed the 6000° K. Planckian curve for all wave-lengths beyond 1.25 $\mu$. Radiation at wave-lengths beyond 2.3 $\mu$ is strongly absorbed by $H_2O$ and $CO_2$ and is so weak in any case, that no satisfactory measurements are available.[12] Abbot concludes [13] from existing data that the radiant energy for $\infty > \lambda > 2.5$ is almost exactly 2 per cent. of the total. Because of this low value, the exact form of curve assumed beyond 2.5 $\mu$ will have little influence on the

[12] See, however, Smithsonian Institution, *Annals of Astrop. Obs.*, 5, 1932, p. 104.

[13] Ibid., 5, 1932, p. 105.

results and the Planckian form appears to be the simplest representation.

It is interesting to note that the maximum spread of the experimental points in the visible and near infrared is generally not more than 10 per cent., while the solid and the dotted curves differ by 5 per cent. or less. At wave-lengths longer than 1.0 $\mu$ and at wave-lengths shorter than 0.4 $\mu$, the scattering of points is much greater and differences of as much as 50 per cent. are found.

Consideration of all data led to the tentative adoption of the heavy curve shown in Fig. 1. The integral,

$$G = 1322 = k \int_0^\infty G_{\lambda\,\mathrm{rel}} d\lambda, \qquad (1)$$

for this curve was evaluated mechanically. In this way, the scale factor $k$ was found to be 3.756. Multiplication of the ordinates of the heavy curve of Fig. 1 by this value of $k$ gave the actual irradiation $G$ in watt m.$^{-2}$ per micron. These values are given in Fig. 2 and Table I and are proposed as a standard for use in engineering computations dealing with solar irradiation.

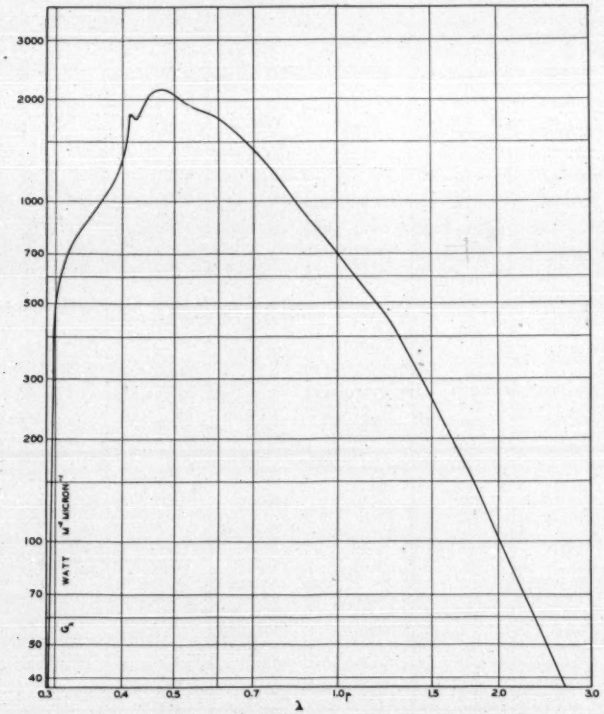
For the sake of definiteness, I have brought the curve down to zero at 0.290 $\mu$. The actual solar curve outside our atmosphere is not zero at this wave-length, though there is evidence that the actual irradiation is very low. Experimental difficulties are great, however, since atmospheric ozone causes almost complete absorption at 0.290 so that it is difficult if not impossible to determine how much of the absorption occurs in the earth's atmosphere and how much in the sun. This distinction may worry the astrophysicist; but it should cause no trouble in the present paper, where the curve is used merely as a convenient norm from which irradiation of the earth's surface is obtained.

#### 4. ATMOSPHERIC SCATTERING.

The direct radiation from the sun is attenuated by the scattering effect of molecules of nitrogen, oxygen, and other constituents of the atmosphere. Since the molecular size is very small compared with the wave-lengths under consideration, the Rayleigh fourth-power relation should apply. That

it does apply was shown by Fowle,[14] who was able to obtain a fairly precise determination of Loschmidt's number by sub-

FIG. 2.




Proposed standard solar irradiation curve. Watt m.$^{-2}$ micron$^{-1}$ on a surface perpendicular to the sun's rays, outside the atmosphere and at the mean solar distance.

stituting atmospheric transmission data obtained on Mount Wilson in Rayleigh's formula.

[14] F. E. Fowle, "The Atmospheric Scattering of Light," Smithsonian Misc. Coll., 69, No. 3, 1918.

TABLE I.

*Solar Irradiation at Normal Incidence, Outside Atmosphere, and at Mean Solar Distance.*

Solar constant = 1322 watt m.$^{-2}$.

| $\lambda$ (microns) | $G_\lambda$ (watt m$^{-2}$ $\mu^{-1}$) | $\lambda$ (microns) | $G_\lambda$ (watt m$^{-2}$ $\mu^{-1}$) | $\lambda$ (microns) | $G_\lambda$ (watt m$^{-2}$ $\mu^{-1}$) |
|---|---|---|---|---|---|
| 0.290 | 0 | 0.400 | 1304 | 1.0 | 706 |
| 0.291 | 190 | 0.405 | 1427 | 1.1 | 590 |
| 0.292 | 250 | 0.410 | 1728 | 1.2 | 488 |
| 0.293 | 289 | 0.413 | 1803 | 1.3 | 395 |
| 0.294 | 318 | 0.420 | 1766 | 1.4 | 319 |
| | | 0.424 | 1742 | | |
| 0.295 | 345 | 0.430 | 1788 | 1.5 | 260 |
| 0.296 | 368 | 0.440 | 1939 | 1.6 | 214 |
| 0.297 | 389 | | | 1.7 | 177 |
| 0.298 | 410 | 0.45 | 2036 | 1.8 | 148 |
| 0.299 | 430 | 0.46 | 2096 | 1.9 | 124 |
| | | 0.47 | 2119 | | |
| 0.300 | 450 | 0.48 | 2127 | 2.0 | 105 |
| 0.301 | 470 | 0.49 | 2103 | 2.1 | 89.3 |
| 0.302 | 489 | | | 2.2 | 76.4 |
| 0.303 | 507 | 0.50 | 2061 | 2.3 | 65.8 |
| 0.304 | 524 | 0.51 | 2000 | 2.4 | 56.9 |
| | | 0.52 | 1954 | | |
| 0.305 | 540 | 0.53 | 1912 | 2.5 | 49.5 |
| 0.306 | 556 | 0.54 | 1894 | 2.6 | 43.2 |
| 0.307 | 571 | | | 2.7 | 37.9 |
| 0.308 | 586 | 0.55 | 1878 | 2.8 | 33.4 |
| 0.309 | 601 | 0.56 | 1861 | 2.9 | 29.5 |
| | | 0.57 | 1841 | | |
| 0.310 | 616 | 0.58 | 1819 | 3.0 | 26.1 |
| 0.311 | 628 | 0.59 | 1795 | 3.1 | 23.3 |
| 0.312 | 640 | | | 3.2 | 20.8 |
| 0.313 | 652 | 0.60 | 1762 | 3.3 | 18.6 |
| 0.314 | 664 | 0.61 | 1727 | 3.4 | 16.6 |
| | | 0.62 | 1690 | | |
| 0.315 | 676 | 0.63 | 1653 | 3.5 | 14.9 |
| 0.316 | 686 | 0.64 | 1616 | 3.6 | 13.5 |
| 0.317 | 696 | | | 3.7 | 12.2 |
| 0.318 | 706 | 0.65 | 1579 | 3.8 | 11.1 |
| 0.319 | 716 | 0.66 | 1543 | 3.9 | 10.1 |
| | | 0.67 | 1508 | | |
| 0.320 | 726 | 0.68 | 1473 | 4.0 | 9.20 |
| 0.325 | 762 | 0.69 | 1439 | 4.1 | 8.44 |
| 0.330 | 796 | | | 4.2 | 7.75 |
| 0.335 | 826 | 0.70 | 1405 | 4.3 | 7.10 |
| 0.340 | 856 | 0.71 | 1371 | 4.4 | 6.50 |
| 0.345 | 886 | 0.72 | 1337 | | |
| | | 0.73 | 1304 | 4.5 | 5.93 |
| 0.350 | 916 | 0.74 | 1270 | 4.6 | 5.44 |
| 0.360 | 976 | | | 4.7 | 4.99 |
| 0.370 | 1046 | 0.75 | 1236 | 4.8 | 4.62 |
| 0.380 | 1121 | 0.80 | 1097 | 4.9 | 4.32 |
| 0.390 | 1202 | 0.85 | 976 | | |
| | | 0.90 | 871 | 5.0 | 4.06 |
| | | 0.95 | 781 | | |

The study of a large number of data allowed Fowle [15] to separate the scattering effect of water vapor from true atmospheric scattering. The transmission factor of the atmosphere directly above Mount Wilson and with no water vapor may be written

$$\tau_{a\lambda} = 10^{-k_{a\lambda}}, \qquad (2)$$

where $k_{a\lambda}$ is a function of wave-length. The values of $k_{a\lambda}$, obtained from the experimental values of $\tau_{a\lambda}$, are plotted against wave-length in Fig. 3. Fowle found that between 0.35 and 0.50 $\mu$, the values plotted as a straight line having a slope of $-4$, as would be expected from Rayleigh's theory. At wave-lengths from 0.5 to 0.7 $\mu$, the points depart from the straight line because of the Chappuis ozone band, while at wave-lengths beyond 1 $\mu$ the transmission factor is so nearly unity that experimental errors make the points completely unreliable. There is every reason to believe, however, that the Rayleigh relation continues to apply at all wave-lengths in the solar spectrum, so that the transmission factor associated with atmospheric scattering may be written

$$\tau_{a\lambda} = 10^{-0.00380/\lambda^4}, \qquad (3)$$

where $\lambda$ is in microns. Eq. (3) applies when the sun is at the zenith and the barometric pressure is 760 mm.

I have also plotted (Fig. 3) Fowle's values for the scattering effect of water vapor. In this case the curve has a slope of $-2$ instead of $-4$; and the associated transmission factor may be written

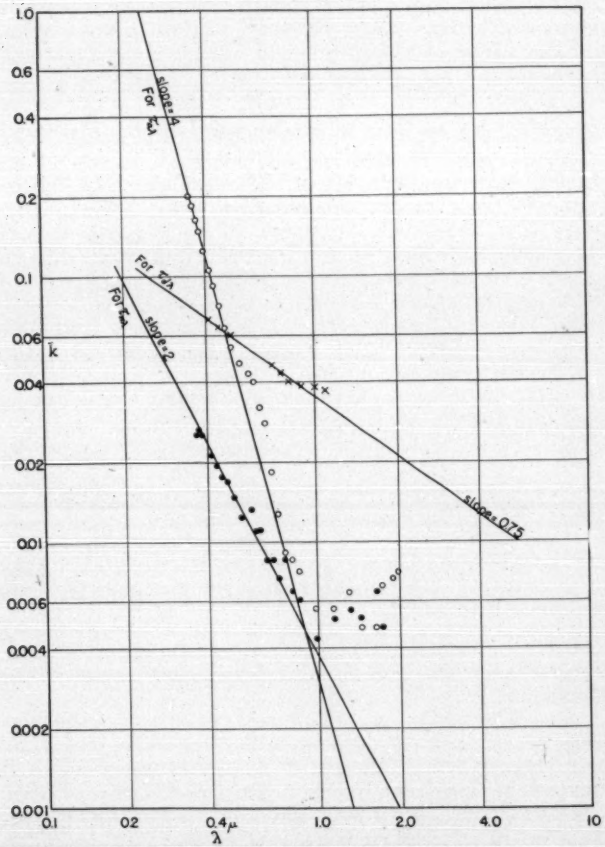
$$\tau_{w\lambda} = 10^{-0.0075/\lambda^2}. \qquad (4)$$

for zenith sun and with 20 mm. of precipitable water above the station.

At an elevation of 1000 m. or more, these two transmission factors are usually sufficient to account for all the observable scattering of light. When dust is present, however, as it always is near sea level, it will introduce additional scattering. The particles are rather large (order of 1 $\mu$ diameter) so that the effect of wave-length is less marked than with molecular scattering, and it is customary to assume that scattering by

[15] F. E. Fowle, "Avogadro's Constant and Atmospheric Transparency," *Astrop. J.*, 40, 1914, p. 435.

FIG. 3.




Atmospheric scattering. Values of $k$ in the equation:
$\tau_\lambda = 10^{-k}$.

dust is independent of λ. A more thorough analysis is shown in Fig. 3. Eqs. (3) and (4) were used in calculating the total transmission factor $\tau_\lambda$ at sea level and for 20 mm. of precipitable water. The resulting curve was compared with the mean curve obtained at Washington, D. C.[16] The ratio between the ordinates of the two curves was attributed to dust, and the corresponding values of $k_{d\lambda}$ were plotted in Fig. 3. The slope is seen to be $-0.75$ and the accompanying transmission factor is

$$\tau_{d\lambda} = (10)^{-0.0353/\lambda^{0.75}}. \tag{5}$$

According to Hand,[17] the average number of dust particles at Washington is approximately 800 per cubic cm.; so for a first approximation one can associate Eq. (5) with 800 particles/cm.$^3$ and can calculate $\tau_{d\lambda}$ for other amounts of dust by proportionate changes in the exponent.

The total effect of scattering is, by the Bouguer relation,

$$\tau_\lambda = [(\tau_{a\lambda})^{p/760}(\tau_{w\lambda})^{w/20}(\tau_{d\lambda})^{d/800}]^m, \tag{6}$$

where $\tau_{a\lambda}$ = spectral transmission factor associated with scattering by a dry atmosphere at 760 mm. pressure and with sun at zenith,

$\tau_{w\lambda}$ = spectral transmission factor associated with scattering by water vapor, for 20 mm. of precipitable water directly above the observer,

$\tau_{d\lambda}$ = spectral transmission factor associated with dust, for 800 particles/cm$^3$ at the level of the observer, and with sun at zenith,

$p$ = barometric pressure (mm.),

$w$ = depth of precipitable water (mm.),

$m$ = sec $\theta$ = air mass ($m$ = 1 for sun at zenith),

$\theta$ = zenith angle of sun.

A convenient way of obtaining $\tau_\lambda$ from Eq. (6) is to plot the three separate factors on logarithmic paper. A pair of dividers can then be used to obtain the sum of the three distances below the line $\tau$ = 1, giving the curve of $\tau_\lambda$ vs. λ, which can be plotted very rapidly in this manner.

[16] Smithsonian Institution, *Annals of Astrop. Obs.*, **2**, 1908, p. 113.

[17] I. F. Hand, Review of United States Weather Bureau Solar Radiation Investigations, *Mon. Weather Rev.*, 65, 1937, Table 12, p. 441.

### 5. OZONE.

The measured transmission curves for the atmosphere contain also the effect of *absorption* of radiant energy by ozone. The transmission factor associated with the Chappuis band (0.5 to 0.7 $\mu$) was taken from Wulf,[18] who made these measurements in the solar spectrum with a layer of ozone equivalent to 3.8 mm. at normal temperature and pressure. The results (smoothed) are given in Table II.

At shorter wave-lengths, the Hartley band and the Huggins band extend to approximately 0.35 $\mu$. These data (Table II) are based on the research of Läuchli.[19] It has not been settled definitely if appreciable error is introduced by applying the Bouguer formula to these data in finding the effect of a change in the amount of the ozone. The formula has been used by many investigators,[19,20] however, and with good results. It will be used in the present paper.

### 6. COMPARISON OF COMPUTED AND MEASURED TRANSMISSION CURVES.

The heavy curve of Fig. 4 was computed by use of the formulas and data of the preceding sections and for a barometric pressure of 760 mm., 20 mm. of precipitable water, 800 dust particles/cm.$^3$, and 3.8 mm. of ozone. The Smithsonian results for Washington [16] are in good agreement except at wave-lengths below 0.4 $\mu$, where they are probably in error because of stray light in the monochromator. The two solid circles are measurements of Fabry and Buisson [10] at Marseille, France. Since this is also an industrial city only slightly above sea level, the results should be comparable with those obtained at Washington.

A more complete comparison between the theoretical curve and the results of Fabry and Buisson is shown in Fig. 5. The experimental results are slightly above the curve, which

[18] O. R. Wulf, "The Determination of Ozone by Spectrobolometric Measurements," Smithsonian Misc. Coll., **85**, No. 9, 1931, p. 9.

[19] A. Läuchli, "Zur Absorption der ultravioletten Strahlung im Ozon," *Zs. f. Phys.*, **53**, 1929, p. 92.

[20] Fabry and Buisson, "L'absorption de l'ultra-violet par l'ozone et la limite du spectre solaire," *J. de Phys.*, **3**, 1913, p. 196. F. E. Fowle, "Atmospheric Ozone," Smithsonian Misc. Coll., **81**, No. 11, 1929. R. W. Ladenburg, "Light Absorption and Distribution of Atmospheric Ozone," *J. O. S. A.*, **25**, 1935, p. 259.

TABLE II.

*Transmission Factor for Ozone.**
(3.8 mm. layer at 760 mm. pressure and 0° C.)

| λ (microns) | $a$ | $r_\lambda$ | λ | $a$ | $r_\lambda$ |
|---|---|---|---|---|---|
| 0.290 | 1.65 | $5.38 \times 10^{-7}$ | 0.350 | 0.0008 | 1.000 |
| 0.291 | 1.46 | $2.82 \times 10^{-6}$ | | | |
| 0.292 | 1.29 | $1.26 \times 10^{-5}$ | 0.48 | | 1.000 |
| 0.293 | 1.11 | $6.03 \times 10^{-5}$ | 0.49 | | 0.999 |
| 0.294 | 1.00 | $1.59 \times 10^{-4}$ | | | |
| 0.295 | 0.89 | $4.17 \times 10^{-4}$ | 0.50 | | 0.996 |
| 0.296 | 0.79 | 0.00100 | 0.51 | | 0.993 |
| 0.297 | 0.70 | 0.00219 | 0.52 | | 0.989 |
| 0.298 | 0.61 | 0.00480 | 0.53 | | 0.984 |
| 0.299 | 0.52 | 0.0105 | 0.54 | | 0.979 |
| 0.300 | 0.460 | 0.0178 | 0.55 | | 0.973 |
| 0.301 | 0.405 | 0.0288 | 0.56 | | 0.965 |
| 0.302 | 0.360 | 0.0427 | 0.57 | | 0.960 |
| 0.303 | 0.315 | 0.0631 | 0.58 | | 0.955 |
| 0.304 | 0.275 | 0.0890 | 0.59 | | 0.950 |
| 0.305 | 0.241 | 0.122 | 0.60 | | 0.955 |
| 0.306 | 0.213 | 0.155 | 0.61 | | 0.960 |
| 0.307 | 0.190 | 0.190 | 0.62 | | 0.965 |
| 0.308 | 0.164 | 0.238 | 0.63 | | 0.973 |
| 0.309 | 0.144 | 0.283 | 0.64 | | 0.979 |
| 0.310 | 0.126 | 0.332 | 0.65 | | 0.984 |
| 0.311 | 0.112 | 0.376 | 0.66 | | 0.989 |
| 0.312 | 0.099 | 0.421 | 0.67 | | 0.993 |
| 0.313 | 0.087 | 0.467 | 0.68 | | 0.996 |
| 0.314 | 0.076 | 0.515 | 0.69 | | 0.999 |
| 0.315 | 0.066 | 0.561 | 0.70 | | 1.000 |
| 0.316 | 0.057 | 0.607 | | | |
| 0.317 | 0.050 | 0.645 | | | |
| 0.318 | 0.044 | 0.680 | | | |
| 0.319 | 0.039 | 0.711 | | | |
| 0.320 | 0.0345 | 0.740 | | | |
| 0.325 | 0.0180 | 0.855 | | | |
| 0.330 | 0.0092 | 0.922 | | | |
| 0.335 | 0.0048 | 0.960 | | | |
| 0.340 | 0.0025 | 0.980 | | | |
| 0.345 | 0.0013 | 0.990 | | | |

*From data of Läuchli, Zs. f. Phys., 53, 1929, p. 92, and Wulf, Sm. Misc. Coll., 85, No. 9, 1931, p. 9. The transmission factor is

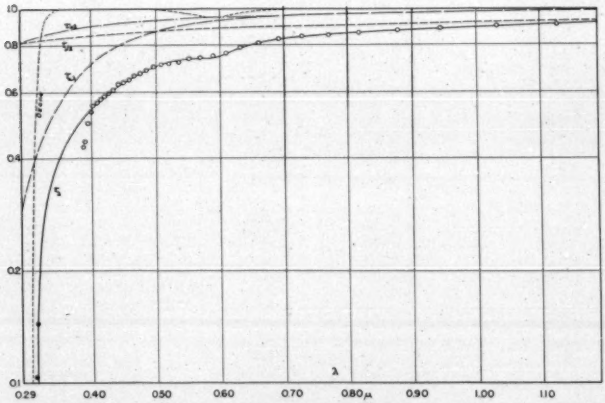
$$r_\lambda = (10)^{-ax}$$

where $x$ is the thickness (NTP) in mm.

probably indicates a smaller amount of ozone than the 3.8 mm. used in the calculations.

Another check for the calculated curve in the ultraviolet is obtained by using the experimental results of Pettit.[9] These measurements were made at Tucson, Arizona (760 m.) in May 1931. Pettit gives the ozone as 1.8 mm. but does not state the amount of water or dust. An assumption of 10 mm.

FIG. 4.



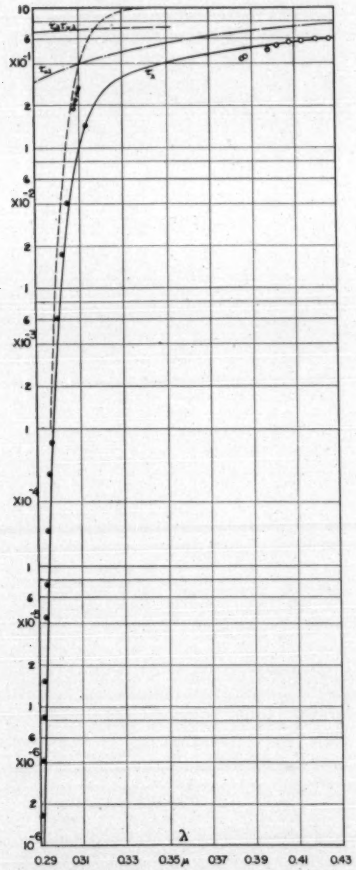

Atmospheric transmission factor for zenith sun.
○ Experimental (Abbot)
——— Calculated for $p$ = 760 mm., $w$ = 20 mm., $d$ = 800, ozone = 3.8 mm.

$H_2O$ and no dust gives the heavy curve of Fig. 6. The points are in good agreement except at the shortest wave-lengths.

Another case is shown in Fig. 7, where the points represent mean values obtained on Mount Whitney, California [21] (4420 m.). At this elevation there is no dust and practically no water vapor. The mean value of 0.8 mm. of precipitable water [22] has almost negligible effect and was omitted from the calculations. The points are seen to hug the calculated curve of $\tau_{o\lambda}$ except in the ozone bands. Other data, obtained in

[21] *Smithsonian Astrop. Obs.*, 3, 1913, p. 136.
[22] Ibid., p. 113.

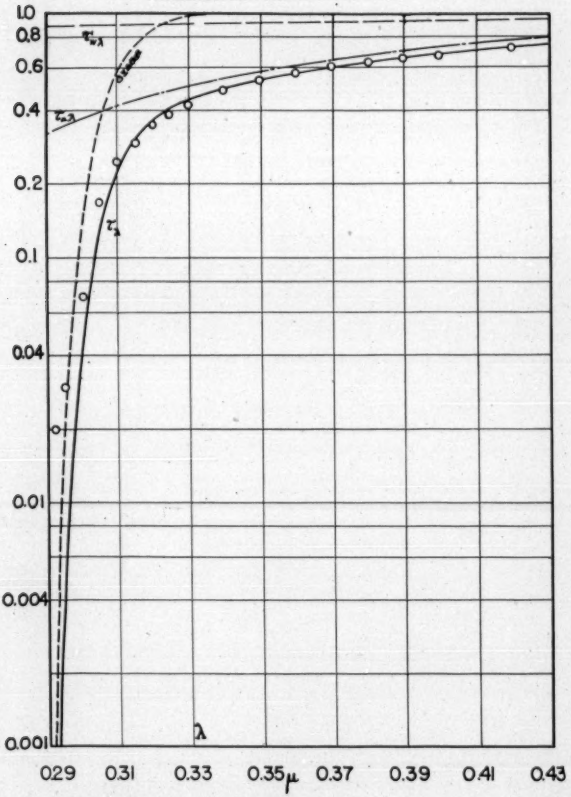
FIG. 5.




Atmospheric transmission factor for zenith sun.

○ Experimental, Abbot
● Experimental, Fabry & Buisson
——— Calculated for $p$ = 760 mm., $w$ = 20 mm., $d$ = 800, ozone = 3.8 mm.

FIG. 6.



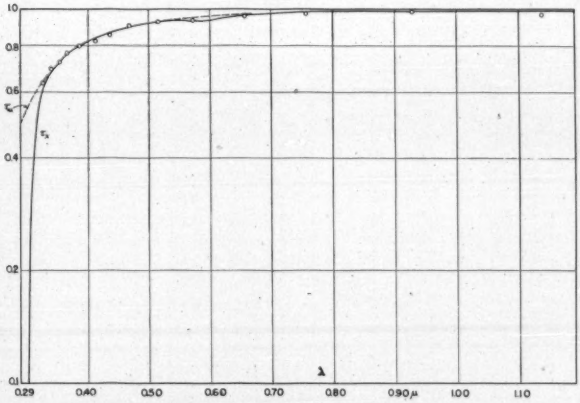

Atmospheric transmission factor for zenith sun.
○ Experimental, Tucson, Arizona (Pettit)
—— Calculated for $p$ = 700 mm., $w$ = 10 mm., $d$ = 0, ozone = 1.8 mm.

various parts of the world, have been checked in a similar manner; but the foregoing examples are sufficient to show the adequacy of the method.

### 7. ATMOSPHERIC ABSORPTION.

The principal absorption of solar radiant energy in the earth's atmosphere occurs in the ozone bands at short wave-

FIG. 7.




Atmospheric transmission factor for zenith sun.
○ Experimental, Mount Whitney (Abbot)
—— Calculated for $p$ = 440 mm., $w$ = 0, $d$ = 0, ozone = 1.8 mm.

lengths and in the water-vapor bands in the infrared. Ozone absorption was considered in Section 5, while the present section will treat of water-vapor absorption, which was disregarded in the transmission curves of Section 6.

Fowle's data [23] on infrared absorption bands are plotted in Fig. 8. Beyond 2.3 $\mu$, there is such strong absorption [24] by $H_2O$ and $CO_2$ that hardly any solar radiation is transmitted.

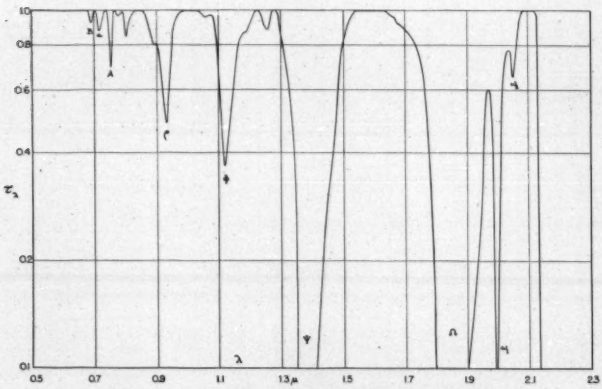
[23] F. E. Fowle, "The Transparency of Aqueous Vapor," *Astrop. J.*, **42**, 1915, Fig. 2, p. 397.

[24] F. E. Fowle, "Water-vapor Transparency to Low-temperature Radiation," Smithsonian Misc. Coll., **68**, No. 8, 1917, Fig. 7, p. 23.

I shall assume that the transmitted energy at wave-lengths beyond 2.3 $\mu$ is negligible in comparison with that at shorter wave-lengths.

The results on absorption are less satisfactory than those on scattering for two reasons. In the first place, the shape of the curve depends to some extent upon the instrument used in the measurements, particularly on the slit width of the monochromator. As the resolution is increased, the depressions in the curve become more numerous, narrower, and

FIG. 8.




Transmission factor associated with absorption by water vapor (Fowle).

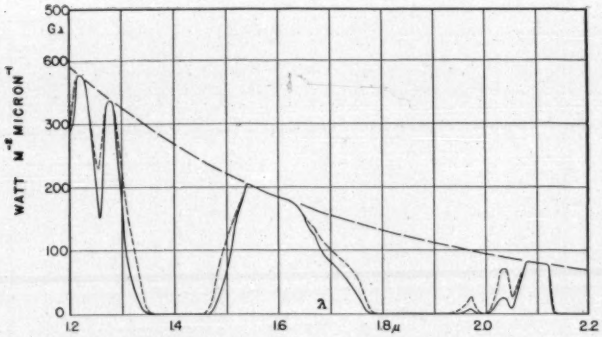
deeper.[25] This leads to the second difficulty: Bouguer's formula does not apply exactly to the data obtained with the wide slits used in spectroradiometric practice.[23]

Fowle obtained an empirical relation [23] between the apparent transmission factor at the bottom of the $\rho$-band and the depth of precipitable water in the atmosphere. There is still no information on how the *shape* of the transmission curve for this band varies with the amount of water vapor. I have assumed, however, that Fowle's empirical relation holds for all

[25] Abbot and Freeman, "Absorption Lines of the Infrared Solar Spectrum," Smithsonian Misc. Coll., **82**, No. 1, 1929.

points in all the water-vapor bands and have obtained on this basis the upper curve of Fig. 9. The lower curve is obtained on the assumption that the Bouguer relation holds. Both curves are for sea level with 20 mm. of precipitable water directly above the station and with an air mass of 5, which is the worst condition considered in this paper. It is likely that the actual results would lie between these two extremes. In view of the small difference in areas resulting from the two assumptions, it seems advisable to use the simple Bouguer

FIG. 9.




Calculated irradiation for $m = 5$.

---- Fowle's method
——— Bouguer formula

relation rather than the more complicated empirical method of Fowle. Thus the Bouguer formula will be used throughout this paper in obtaining the effect of changes in water vapor, ozone, etc.

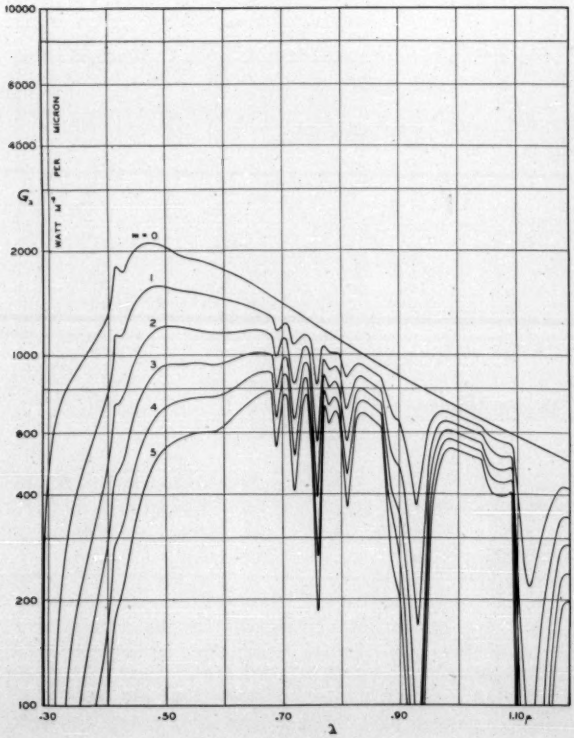
### 8. FINAL IRRADIATION CURVES.

Data and methods are now ready for the calculation of solar irradiation curves for any location and for any amount of water vapor, ozone, and dust in the atmosphere. The most useful results would be for a station near sea level. Accordingly, curves have been calculated for the following

condition:

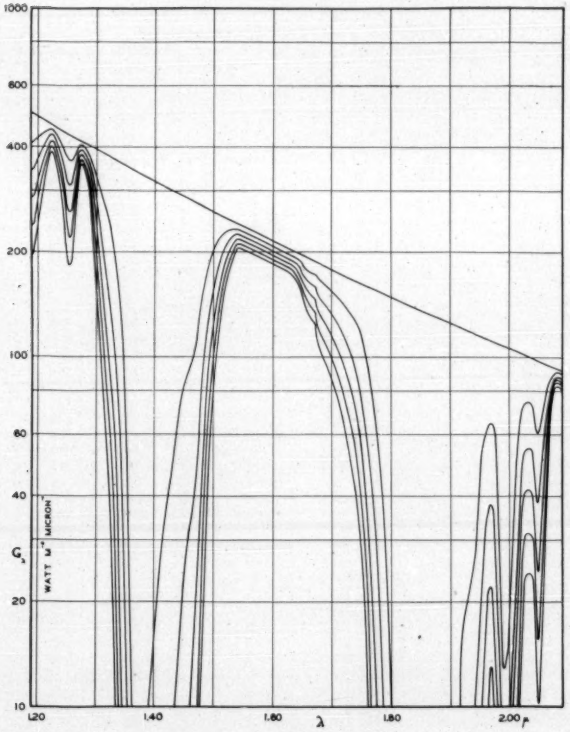
$p$ = 760 mm.,
$w$ = 20 mm.,
$d$ = 300 particles/cm.$^3$,
Ozone = 2.8 mm.,
$m$ = 1, 2, 3, 4, and 5.

FIG. 10.




V. 19

FIG. 10—*Continued.*




Solar irradiation at sea level, proposed standard curves.
$p$ = 760 mm.
$w$ = 20 mm.
$d$ = 300
ozone = 2.8 mm.

This condition differs from that of Fig. 4 in the amounts of dust and ozone, which have been reduced to what appears to be more characteristic of the United States and Europe. The Smithsonian data of Fig. 4 are distinctly too low to check

TABLE III.

*Solar Irradiation at Sea Level with Surface Perpendicular to Sun's Rays, m = 2.*
(Watts per square meter per micron).

| λ (microns) | $G_\lambda$ | λ (microns) | $G_\lambda$ | λ (microns) | $G_\lambda$ |
|---|---|---|---|---|---|
| 0.295 | $2.09\times10^{-4}$ | 0.50 | 1215 | 0.90 | 480 |
| 0.296 | 8.35 | 0.51 | 1206 | 0.91 | 375 |
| 0.297 | $2.87\times10^{-3}$ | 0.52 | 1199 | 0.92 | 258 |
| 0.298 | 9.87 | 0.53 | 1188 | 0.93 | 169 |
| 0.299 | 0.0346 | 0.54 | 1198 | 0.94 | 278 |
| 0.300 | 0.0810 | 0.55 | 1190 | 0.95 | 487 |
| 0.301 | 0.177 | 0.56 | 1182 | 0.96 | 584 |
| 0.302 | 0.342 | 0.57 | 1178 | 0.97 | 633 |
| 0.303 | 0.647 | 0.58 | 1168 | 0.98 | 645 |
| 0.304 | 1.16 | 0.59 | 1161 | 0.99 | 643 |
| 0.305 | 1.91 | 0.60 | 1167 | 1.00 | 630 |
| 0.306 | 2.89 | 0.61 | 1168 | 1.01 | 620 |
| 0.307 | 4.15 | 0.62 | 1165 | 1.02 | 610 |
| 0.308 | 6.11 | 0.63 | 1176 | 1.03 | 601 |
| 0.309 | 8.38 | 0.64 | 1175 | 1.04 | 592 |
| 0.310 | 11.0 | 0.65 | 1173 | 1.05 | 551 |
| 0.311 | 13.9 | 0.66 | 1166 | 1.06 | 526 |
| 0.312 | 17.2 | 0.67 | 1160 | 1.07 | 519 |
| 0.313 | 21.0 | 0.68 | 1149 | 1.08 | 512 |
| 0.314 | 25.4 | 0.69 | 978 | 1.09 | 514 |
| 0.315 | 30.0 | 0.70 | 1108 | 1.10 | 252 |
| 0.316 | 34.8 | 0.71 | 1070 | 1.11 | 126 |
| 0.317 | 39.8 | 0.72 | 832 | 1.12 | 69.9 |
| 0.318 | 44.9 | 0.73 | 965 | 1.13 | 98.3 |
| 0.319 | 49.5 | 0.74 | 1041 | 1.14 | 164 |
| 0.32 | 54.0 | 0.75 | 867 | 1.15 | 216 |
| 0.33 | 101 | 0.76 | 566 | 1.16 | 271 |
| 0.34 | 151 | 0.77 | 968 | 1.17 | 328 |
| | | 0.78 | 907 | 1.18 | 346 |
| 0.35 | 188 | 0.79 | 923 | 1.19 | 344 |
| 0.36 | 233 | | | | |
| 0.37 | 279 | 0.80 | 857 | 1.20 | 373 |
| 0.38 | 336 | 0.81 | 698 | 1.21 | 402 |
| 0.39 | 397 | 0.82 | 801 | 1.22 | 431 |
| | | 0.83 | 863 | 1.23 | 420 |
| 0.40 | 470 | 0.84 | 858 | 1.24 | 387 |
| 0.41 | 672 | | | | |
| 0.42 | 733 | 0.85 | 839 | 1.25 | 328 |
| 0.43 | 787 | 0.86 | 813 | 1.26 | 311 |
| 0.44 | 911 | 0.87 | 798 | 1.27 | 381 |
| | | 0.88 | 614 | 1.28 | 382 |
| 0.45 | 1006 | 0.89 | 517 | 1.29 | 346 |
| 0.46 | 1080 | | | | |
| 0.47 | 1138 | | | | |
| 0.48 | 1183 | | | | |
| 0.49 | 1210 | | | | |

TABLE III.—*Continued.*

| λ (microns) | $G_\lambda$ | λ (microns) | $G_\lambda$ | λ (microns) | $G_\lambda$ |
|---|---|---|---|---|---|
| 1.30 | 264 | 1.60 | 202 | 1.90 | — |
| 1.31 | 208 | 1.61 | 198 | 1.91 | 0.705 |
| 1.32 | 168 | 1.62 | 194 | 1.92 | 2.34 |
| 1.33 | 115 | 1.63 | 189 | 1.93 | 3.68 |
| 1.34 | 58.1 | 1.64 | 184 | 1.94 | 5.30 |
| 1.35 | 18.1 | 1.65 | 173 | 1.95 | 17.7 |
| 1.36 | 0.660 | 1.66 | 163 | 1.96 | 31.7 |
| 1.37 | — | 1.67 | 159 | 1.97 | 37.7 |
| 1.38 | — | 1.68 | 145 | 1.98 | 22.6 |
| 1.39 | — | 1.69 | 139 | 1.99 | 1.58 |
| 1.40 | — | 1.70 | 132 | 2.00 | 2.66 |
| 1.41 | 1.91 | 1.71 | 124 | 2.01 | 19.5 |
| 1.42 | 3.72 | 1.72 | 115 | 2.02 | 47.6 |
| 1.43 | 7.53 | 1.73 | 105 | 2.03 | 55.4 |
| 1.44 | 13.7 | 1.74 | 97.1 | 2.04 | 54.7 |
| 1.45 | 23.8 | 1.75 | 80.2 | 2.05 | 38.3 |
| 1.46 | 30.5 | 1.76 | 58.9 | 2.06 | 56.2 |
| 1.47 | 45.1 | 1.77 | 38.8 | 2.07 | 77.0 |
| 1.48 | 83.7 | 1.78 | 18.4 | 2.08 | 88.0 |
| 1.49 | 128 | 1.79 | 5.70 | 2.09 | 86.8 |
| 1.50 | 157 | 1.80 | 0.920 | 2.10 | 85.6 |
| 1.51 | 187 | 1.81 | — | 2.11 | 84.4 |
| 1.52 | 209 | 1.82 | — | 2.12 | 83.2 |
| 1.53 | 217 | 1.83 | — | 2.13 | 20.7 |
| 1.54 | 226 | 1.84 | — | 2.14 | — |
| 1.55 | 221 | 1.85 | — | | |
| 1.56 | 217 | 1.86 | — | | |
| 1.57 | 213 | 1.87 | — | | |
| 1.58 | 209 | 1.88 | — | | |
| 1.59 | 205 | 1.89 | — | | |

either the Potsdam data [26] or various results obtained at the National Bureau of Standards; but if the dust is reduced to 3/8 its previous value (which was rather arbitrarily identified with 800 particles/cm.$^3$) a reasonably good agreement is obtained.

The calculated curves are shown in Fig. 10, and the data are assembled in Table III. The results are given for five values of air mass and can thus be used in obtaining the

[26] G. Müller, "Die Extinktion des Lichtes im der Erdatmosphäre und die Energieverteilung im Sonnenspektrum," Astrop. Obs. Potsdam, *Publ.*, **22**, No. 64, 1912.

irradiation or illumination at any hour of the day except near sunrise or sunset. *It is suggested that the curve for air mass 2 be used whenever a single, standard solar-radiation curve is needed in engineering calculations for places near sea level.*

If further refinement is needed, the other curves of Fig. 10 may be employed to take into account the exact zenith angle of the sun at the particular time under consideration. The amount of ozone and dust is believed to be a good average for Europe and America, while the amount of water-vapor is characteristic of summer or spring rather than winter. In some cases, it may be advisable to calculate similar curves for more water vapor (or less); and if a large amount of dust or smoke is present, suitable allowance must be made for its effect. It is believed, however, that the curves of Fig. 10 will be sufficient for most engineering purposes.[27]

### 9. TOTAL IRRADIATION.

If the curves of Fig. 10 are to be useful, they must give values of total irradiation, illumination, etc., that are in agreement with direct measurements. The remaining sections of this paper will be devoted to the comparison of calculated values with data obtained by direct measurements made by independent observers. Checks will be obtained on the following:

(1) Total irradiation (watt $m.^{-2}$) on a surface perpendicular to the sun's rays.
(2) Irradiation (watt $m.^{-2}$) in the extreme ultraviolet part of the solar spectrum.
(3) Time required for minimum perceptible erythema.
(4) Illumination (lumen $m.^{-2}$) on a surface perpendicular to the sun's rays.
(5) Color of direct sunlight.

Total irradiation is obtained by evaluating the areas under the curves of Fig. 10. The results are assembled in Table IV.

[27] Curves of a similar nature have been obtained by: H. H. Kimball, *C. I. E. Proc.*, 1928, p. 501; Forsythe and Christison, *J. O. S. A.*, **20**, 1930, p. 396; F. S. Brackett, "Biological Effect of Radiation," New York, 1936, Vol. I, Chap. IV; P. Moon, "Scientific Basis of Illuminating Engineering," New York, 1936, pp. 29, 30; H. P. Gage, *I. E. S. Trans.*, **34**, 1939, p. 316.

TABLE IV.

*Calculated Solar Irradiation at Sea Level.*

| λ | G (watt m.$^{-2}$) | | | | | |
|---|---|---|---|---|---|---|
| | m = 0 | 1 | 2 | 3 | 4 | 5 |
| 0.29–0.40μ | 94.6 | 40.1 | 19.8 | 10.0 | 5.4 | 2.7 |
| 0.40–0.70 | 540.0 | 419.7 | 327.8 | 258.6 | 205.8 | 163.7 |
| 0.70–1.1 | 365.4 | 309.2 | 267.5 | 233.4 | 205.1 | 181.5 |
| 1.1 –1.5 | 162.5 | 95.3 | 70.4 | 57.0 | 48.1 | 40.7 |
| 1.5 –1.9 | 72.8 | 50.8 | 45.1 | 41.0 | 38.0 | 35.2 |
| 1.9 –∞ | 86.8 | 12.8 | 9.2 | 7.5 | 6.5 | 5.8 |
| Total | 1322 | 927.9 | 739.8 | 607.5 | 508.9 | 429.6 |

When plotted on logarithmic paper, the curve is concave upward (Fig. 11) as has been found experimentally by many investigators. The curve of Fig. 11 was plotted from the calculated data of Table IV. The points are experimental values for months in which the amount of water vapor is approximately the value [28] used in Fig. 10. These experimental results [29] are monthly averages for Washington, D. C., for the years 1914 to 1936, and have been reduced to mean solar distance. A fairly good agreement is noted, except that the experimental results indicate slightly greater curvature than is obtained in the calculated curve.

### 10. ULTRAVIOLET IRRADIATION.

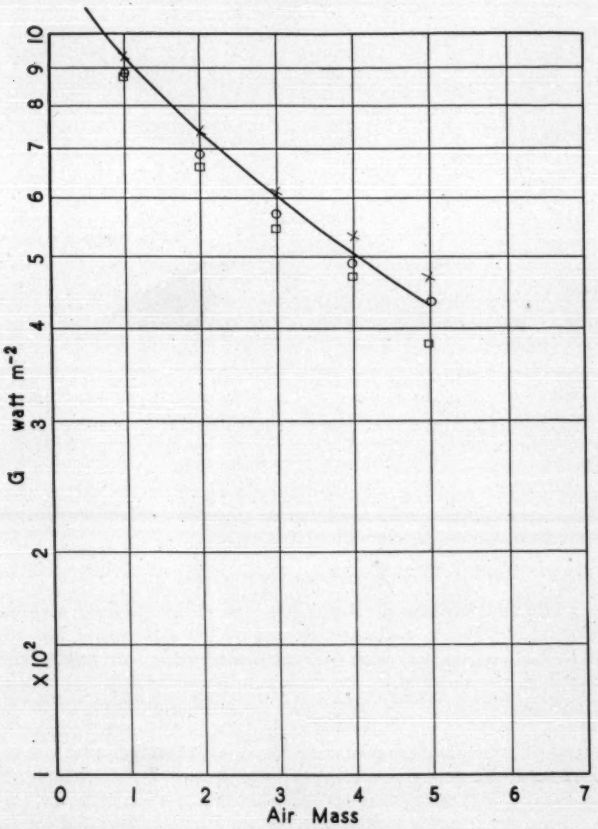
The spectral irradiation curves in the ultraviolet are replotted in Fig. 12. The conditions are the same as for Fig. 10; namely, sea level with 20 mm. of precipitable water, 300 dust particles per cubic cm., and 2.8 mm. (NTP) ozone. An outstanding feature is the very rapid decrease in ultraviolet as the air mass increases. For wave-lengths less than approximately 0.309 μ the greater part of this decrease is produced by ozone; while at longer wave-lengths, scattering by atmospheric molecules and dust particles becomes the preponderant factor.

Figure 13 shows similar irradiation curves calculated for an elevation of 2220 meters. The irradiation is greater than in

[28] H. H. Kimball, "Amount of Solar Radiation that Reaches the Surface of the Earth," *Mo. Weather Rev.*, 58, 1930, p. 51.

[29] *Mo. Weather Rev.*, 65, 1937, p. 438.

FIG. 11.



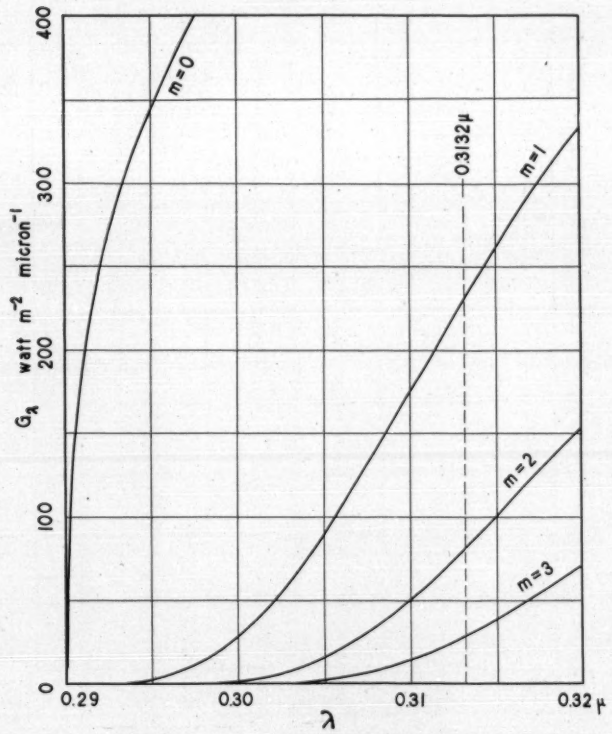

Total irradiation (watt m.$^{-2}$).

Experimental values { ○ May, × April, □ June

Calculated from Fig. 10 ———

the previous case and extends to shorter wave-lengths. These curves are supposed to represent conditions at Flagstaff,

FIG. 12.

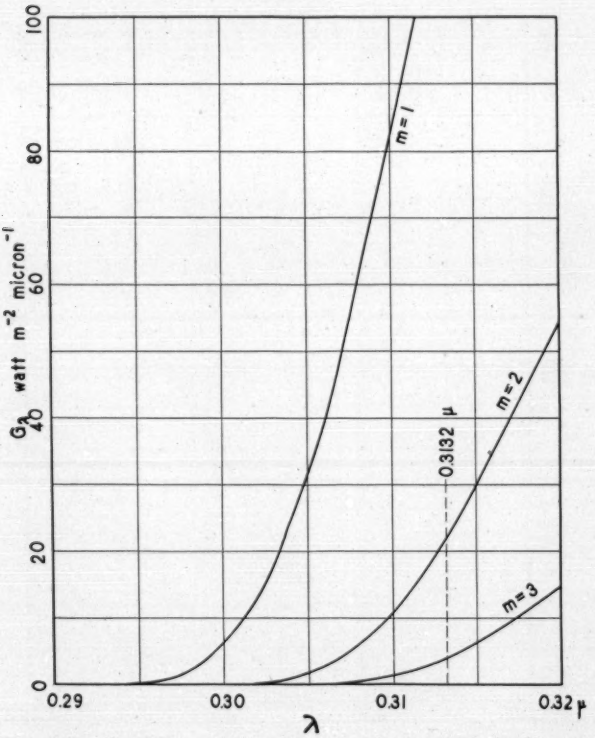



Ultraviolet irradiation, computed for conditions of Fig. 10.

Arizona, and are calculated for a pressure of 580 mm., zero water vapor and zero dust. A value of 1.8 mm. of ozone is used in the computations, since this amount is in agreement

with the measurements of Pettit [9] at Tucson, Arizona, and of Fowle at Harqua Halla.

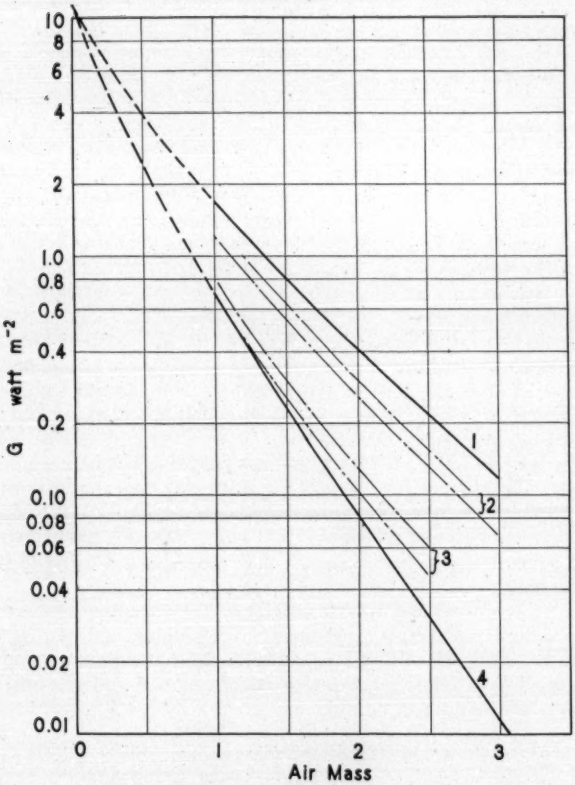
FIG. 13.




Ultraviolet irradiation, computed for $p$ = 580 mm., $w$ = 0, $d$ = 0, ozone = 1.8 mm.

The total irradiation (watts/m.$^2$) for wave-lengths less than 0.3132 $\mu$ was obtained by integration of the curves of Figs. 12 and 13. The values are shown by the circles in Fig. 14. Curves 2 and 3 were obtained experimentally by Coblentz

FIG. 14.




Total irradiation at wave-lengths less than 0.3132μ.

1. Calculated for $p = 580$ mm.
2. Experimental values for Flagstaff, Ariz. (Coblentz).
3. Experimental values for Washington, D. C. (Coblentz).
4. Calculated for $p = 760$ mm.

and Stair[30] at Flagstaff and Washington respectively. The calculated results for Flagstaff are approximately 20 per cent. higher than the experimental results. This discrepancy could be reduced by assuming an appreciable amount of dust and water vapor in the atmosphere, but it is more likely caused by a slightly greater amount of ozone than the assumed value of 1.8 mm. The calculated results for Washington are considerably lower than the experimental values, though almost perfect agreement could be obtained by a slight change in the assumed amount of ozone. The shape of the calculated and experimental curves is gratifyingly similar; and though the numerical check is not very satisfactory, it is probably as good as can be expected at the present state of the art.

Because of the very narrow band of wave-lengths under consideration, one might guess that the curves of Fig. 14 would be straight lines, as they would be for truly homogeneous radiation. In fact, this assumption is made by Coblentz,[31] who extends the line to zero air mass and obtains in this manner an irradiation of 6.0 watt/m.$^2$ outside the atmosphere. Actually, however, the irradiation changes very rapidly in this narrow band of wave-lengths so it is anything but homogeneous. As a result, the curves are distinctly concave upward and the calculated irradiation outside the atmosphere is 10.62 watts/m.$^2$ between 0.2900 and 0.3132 $\mu$. It seems likely that this result is more nearly correct than the value of 6.0 given by Coblentz.

It is interesting also to calculate the time required for minimum perceptible erythema at Washington and at Flagstaff. The curves of Figs. 12 and 13 for $m = 1$ were evaluated according to relative erythemal effectiveness,[32] and the integrals were obtained, giving

Washington, 0.140 erythemalwatts/m.$^2$, $t = 29.8$ minutes,
Flagstaff, 0.410 erythemalwatts/m.$^2$, $t = 10.1$ minutes.

The times ($t$) for MPE were obtained by using the Luckiesh

[30] Coblentz and Stair, "Evaluation of Ultraviolet Solar Radiation of Short Wave-lengths," *B. S. J. R.*, 16, 1936, Fig. 7 (p. 337) and Fig. 11 (p. 343).
[31] Ibid., p. 345.
[32] *C. I. E. Comple Rendu*, 1935, p. 625.

value [33] of 250 erythemalwatt-sec./m.$^2$ for MPE. These calculations are in approximate agreement with Coblentz's experience [34] that MPE was obtained in Washington at noon in midsummer in 20 to 30 minutes, while at Flagstaff only 9 or 10 minutes were required.

### 11. ILLUMINATION AND COLOR.

The proposed standard curves of Table III can be used also in the calculation of direct solar illumination. The data were multiplied by the standard visibility function $v$, and integrals of the form

$$E = \int_0^\infty v G_\lambda d\lambda \qquad \text{(lightwatt m.}^{-2}\text{)}$$

were evaluated. A conversion factor of 621 lumens = 1 lightwatt then gave the illumination values of Table V. These are illuminations for direct sunlight only (no skylight) and are for a surface perpendicular to the sun's rays.

Very few experimental data are available as a check on the calculated results of Table V, since most illumination measurements include the effect of skylight. However, Kimball gives a set of conversion factors [29] which he obtained at Washington by the use of an illuminometer of the visual-comparison type. These factors give the relation between direct solar illumi-

TABLE V.

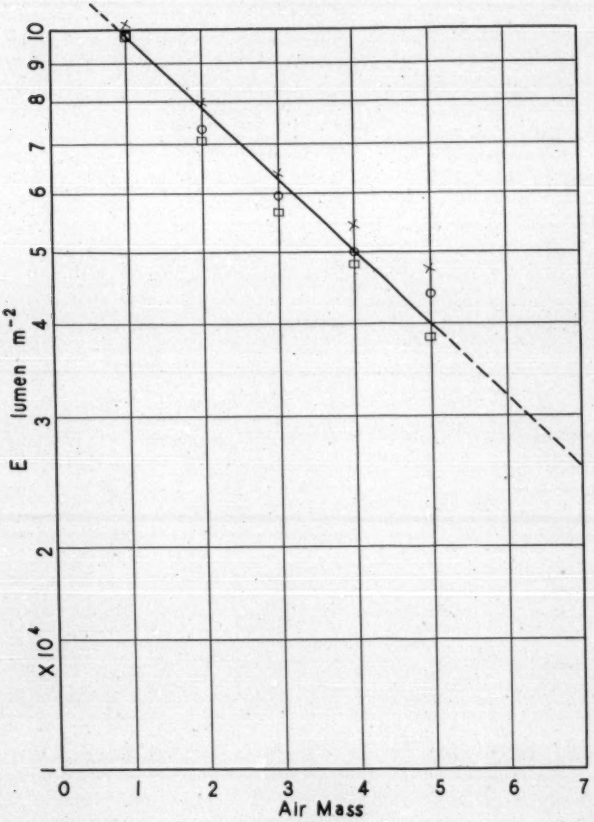
*Calculated Illumination and Color of Direct Sunlight at Sea Level.*

| | $m = 0$ | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| E (lumen m.$^{-2}$) | 123,400 | 98,300 | 78,400 | 62,800 | 50,100 | 40,000 |
| $x$ | 0.3179 | 0.3306 | 0.3431 | 0.3558 | 0.3676 | 0.3803 |
| $y$ | 0.3297 | 0.3437 | 0.3567 | 0.3687 | 0.3789 | 0.3881 |
| $z$ | 0.3524 | 0.3257 | 0.3002 | 0.2755 | 0.2535 | 0.2316 |
| $1/Tc \times 10^{+4}$ | 161.2 | 180.0 | 196.6 | 214.0 | 230.3 | 246.8 |
| $Tc$ (°K) | 6,200 | 5,550 | 5,090 | 4,670 | 4,340 | 4,050 |

[33] Luckiesh and Holladay, "Fundamental Units and Terms for Biologically-effective Radiation," *J. O. S. A.*, **23**, 1933, p. 197.

[34] Coblentz and Stair, "Factors Affecting Ultraviolet Solar-Radiation Intensities," *B. S. J. R.*, **15**, 1935, p. 142.

FIG. 15.



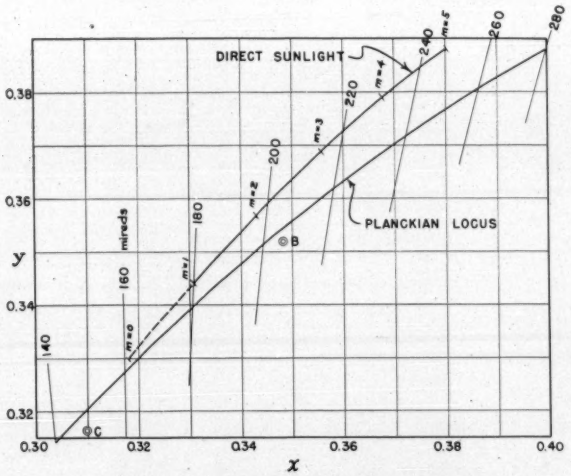

Direct solar illumination (lumen m.$^{-2}$).

Experimental values { ○ May, ⊗ April, □ June

Calculated from Fig. 10 ——

nation and total irradiation for various values of $m$. Multiplication of the previous experimental values of $G$ (Fig. 11) by the Kimball illumination factors gives the points of Fig. 15. The curve is the calculated one, plotted from the data of Table V. It appears to be a perfectly straight line; which does not seem unreasonable, in view of the uniformity of the $G_\lambda$-curves in the visible region. The experimental points

FIG. 16.

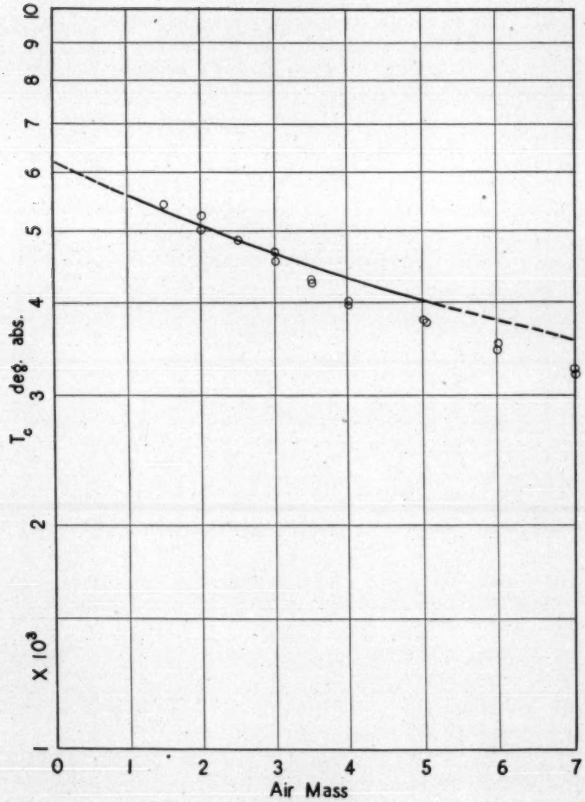



Color of direct sunlight, calculated for sea level by use of Fig. 10.

show a distinct curvature but are otherwise in approximate agreement with the calculated curve.

Table V contains also the coördinates in the color triangle, calculated by use of the C.I.E. standard data. The calculated locus for direct sunlight at sea level is shown in Fig. 16. For sunlight outside the atmosphere, the proposed standard of Table I gives a point ($m = 0$) very close to a Planckian distribution with temperature 6200° K. As the air mass increases, the sunlight becomes progressively further above the Planckian

FIG. 17.




Color temperature of direct sunlight at Washington.
Experimental data of Priest ○
Calculated from Fig. 10 ——

locus, which may explain Priest's difficulty [35] in obtaining a color match between a Planckian distribution and sunlight with low sun.

To obtain the closest color temperature $T_c$ for the six calculated points, I have used the method and data of Judd,[36] as indicated by the lines of equal $(1/Tc)$ drawn in Fig. 16. The curve of Fig. 17 was plotted from the resulting values of $T_c$. Priest's data, obtained at Washington in 1920 by use of the Leucoscope, are shown by the points.[37] These data are not averages, but were obtained during a single day. It is likely that measurements for other days, had they been obtained, would have differed by amounts at least as large as those between the points and curve of Fig. 17.

### 12. SUMMARY.

A wealth of data on sunlight has been obtained by astrophysicists, meteorologists, and others; but this information has been scattered through the literature and has not been generally available to engineers. The present paper correlates some of the data and specifies a proposed standard spectral-distribution curve for sunlight outside the atmosphere. Methods are given also for the calculation of the spectral irradiation curve for any elevation above sea level and for any air mass, and these methods lead to proposed standard curves to be used in engineering calculations dealing with direct sunlight at sea level.

These curves are checked against independent data on total irradiation, ultraviolet irradiation, illumination, and color temperature. In all cases, the agreement between calculated and experimental results gives confidence in the validity of the proposed curves for various engineering applications.

[35] I. G. Priest, "Preliminary Data on the Color of Daylight at Washington," *J. O. S. A.*, **7**, 1923, p. 78.

[36] D. B. Judd, "Estimation of Chromaticity Differences and Nearest Color Temperature on the Standard 1931 I.C.I. Colorimetric Coördinate System," *J. O. S. A.*, **26**, 1936, p. 421.

[37] As given by Kimball, *Mo. Weather Rev.*, **52**, 1924, Fig. 2, p. 475.

**Research on Pearls.**—Dr. A. E. Alexander, until recently holder of the Pearl Fellowship at Mellon Institute, Pittsburgh, Pa., is located in New York with office and laboratory at 665 Fifth Avenue. For the past two years, Dr. Alexander has been working on pearls, seeking to gather complete scientific data on all gems originating in pearl-bearing molluscs. This research program, which was sponsored by Pearl Associates, Inc., a group of leading New York retail and wholesale pearl dealers, yielded a series of publications that are regarded generally as authoritative. Some of the results of this research revealed that not all pearls are composed of the orthorhombic variety of calcium carbonate, aragonite. Several large natural pearls, on sectioning, have been found to be in part of the much commoner hexagonal form of calcium carbonate, calcite. In another part of the work, it was learned that the Japanese cultured pearl possesses a large mother-of-pearl core, which, in representative specimens, averages from 75 to 90 per cent. of the total linear diameter. This finding is at variance with implications in published statements generally accepted by the buying public as valid. Another phase of the research program involved testing equipment in use to distinguish cultured pearls from natural pearls, to lay down methods whereby this equipment could be improved. For quick, accurate determination in which many pearls can be examined at one time, the X-ray fluorescent method is exceedingly useful. The cause of the fluorescence of cultured and fresh water pearls has been shown to lie in the chemical composition. Where internal structural information is desired, the use of soft X-rays may be effectively employed. By this method, an entire pearl necklace can be radiographed in less than one minute, the resulting negative registering in a clear cut manner the internal structural differences that distinguish natural pearls from those that have been cultured.

R. H. O.

# EXTRAGRANULAR FACTORS IN PHOTOGRAPHIC SENSITIVITY.*

BY

S. E. SHEPPARD AND C. L. GRAHAM.

It may be regarded as well established [1] that the primary photolytic action in silver bromide emulsions is that represented by

$$[Br^-] + h\nu \rightarrow Br + \theta,$$

i.e., the removal of an electron from the filled level, consisting of bromide ions, or, equivalently, from lattice-loosened bromide ions. Evidence that the production of photoconductance level electrons is concomitant with the production of free bromine is supplied directly by the photovoltaic studies of Sheppard and Vanselow.[2]

Investigation and theory of the subsequent formation of the latent image have been largely concerned with the transfer of these electrons to neutralize silver ions adjacent to a sensitivity speck, and forming a nucleus of metallic silver, since this was indicated as an essential feature of photographic sensitivity in the "concentration speck" theory. The relatively recent theory of the mechanism proposed by Gurney and Mott [3] regards the "sensitivity speck" as an acceptor for electrons, whereby the negatively charged speck attracts and neutralizes more slowly moving silver ions of the crystal. Whether these silver ions are interstitial or of other origin need not be considered now. This theory has received much support from studies of reciprocity-law failure and of temperature influences on reciprocity-law failure.[4] These studies have tended to show that latent-image formation can be largely divided into a strongly and directly temperature-susceptible part, attributed to the motion of the silver ions, and a much less, or rather indirectly temperature-susceptible part, attributed to the movements and arrests of electrons.[5] It is not proposed to traverse these conclusions, but it is necessary to point out, as indeed has been done before, that

* Communication No. 777 from the Kodak Research Laboratories.

these considerations take no account of the disposal of the freed halogen. The fundamental reaction is *per se* reversible, and the removal and fixation of halogen are of equal moment, for latent-image formation and persistence, with the acceptance and fixation of electrons.

There are three very important factors which influence photographic sensitivity externally to the grain, and which are connected through their influence on halogen removal. These factors are:

i. The pH of the vehicle,
ii. The pAg of the vehicle,
iii. The water content of the vehicle.

The pH of an emulsion has two important but differing functions. One is its influence on the formation of "sensitivity specks"—by accelerating silver sulfide formation and silver reduction. These effects are not reversed by lowering pH. The other important effect, to be considered here, is the reversible pH effect, discovered by Rawling.[6] This consists in an elevation of sensitivity by a rise of pH and a depression of sensitivity by a lowering of pH. The effects of pAg on sensitivity are also twofold, one irreversible, and concerned with sensitivity-speck formation, the other reversible. The latter effect, with gelatino-bromide emulsions, was established by Sheppard and Wightman [7] and its close connection with the reversible pH effect was brought out soon after by Slater Price.[8]

The third effect in question, that of the water content of the vehicle, has been more usually considered as the effect of the "relative humidity" of the atmosphere upon sensitivity.[9] Rather contradictory statements have been made concerning it, in some cases relatively large effects being observed, in others quite small ones.[10] The present investigation shows the reason for this, in demonstrating that all the three factors are closely connected and that only by proper control of this relationship can trustworthy results be obtained.

### ADJUSTMENT OF pAg AND pH.

Adjustments of pAg and pH are made in the liquid emulsion prior to coating and drying, and the values given are

those determined in this at 40° C. The chemical potentials in the "dry" emulsion coatings corresponding to these will be somewhat different numerically * but, since they cannot be measured directly, the precursor values in solution must be used. Actually, an investigation of the electric conductance of "dry" emulsions [11] shows that a potential corresponding to the isoelectric point of lime-processed gelatin remains effective in "dry" gelatin.

In our experiments, pH values were determined with a glass electrode, using a ballistic galvanometer circuit devised by Dr. J. Russell. Since measurements were not required above pH = 9, the sodion error of the glass electrode was not of importance. pAg measurements were made, using the same circuit, with a silver electrode replacing the glass electrode. The circuit is shown diagrammatically in Fig. 1. The cell used for the pAg measurements is shown in Fig. 2. It consists of a saturated calomel half-cell, and a silver electrode in the solution under examination and operated in an air thermostat at 40° C.

The silver electrodes were prepared, following a technique developed by Sheppard, Vanselow and Happ [12] in photovoltaic studies. They were machined out of silver rod stock of specified purity. They are heated to dull redness several times and cooled before original use and this is repeated when contamination, e.g., by mercury, is suspected. From time to time they are cleaned by brushing with a motor-driven steel brush and washing in acetone. This is followed by an occasional cyanide bath for 5 to 10 minutes and an hour or more washing in warm distilled water. When not in use the electrodes are kept in distilled water at 40°. They may be used several weeks without cleaning.

To prevent erratic results, two electrodes were used. They were calibrated directly against silver chloride and bromide sols of known excess halide-ion concentration. These standards were checked occasionally elsewhere in the department by direct e.m.f. determination.

* Gelatin coatings of pH-8 and upwards, also show lower pH values on re dissolving after drying. This is due to absorption of $CO_2$, and may be reduced by buffering.

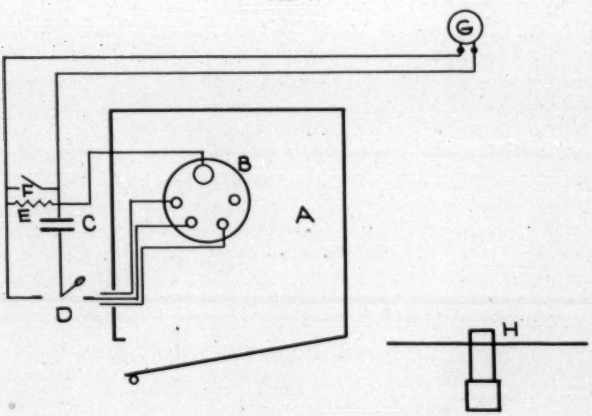
The single potential of the silver electrode at 40° C. is taken as − 0.7965, and that of the saturated calomel half-cell as − 0.2344. The equation used was

$$E_{cell} = E_{Ag} - k \log C - E_{Hg}, \text{ where}$$
$$R \text{ at } 40° \text{ C. is } 0.0621.$$

Hence,

$$pAg = - \log C = \frac{E_{cell} + 0.5621}{- 0.0621}.$$

FIG. 1.

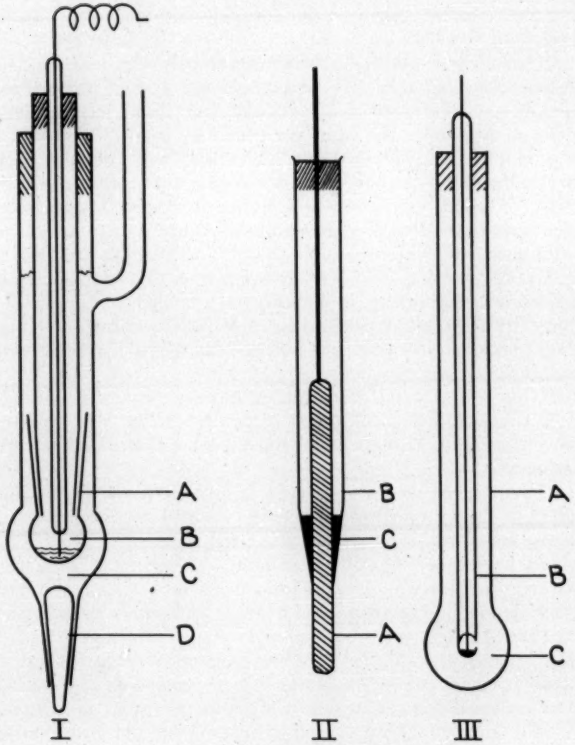



Circuit for pH and pAg Measurement

A. Thermostat.
B. Tenite block.
C. Condenser.
D. Switch.
E. Damping resistance.
F. Switch to stop galvanometer swing.
G. Galvanometer (type H. S.).
H. Scale and telescope.

In general, the pAg value in a silver bromide emulsion will be determined mainly by two factors: the silver ion-halide ion product $[Ag^+][Br^-]$ = constant, and the pH of the gelatin. The first factor is obvious, while the second, in the absence of halogen and other silver-binding ions, increases in magnitude above the isoelectric point, as increasing pH frees amino-

FIG. 2.




I Calomel Half-Cell with Salt Bridge:

A. Ground-glass joint.
B. Saturated calomel half-cell.
C. Potassium nitrate bridge.
D. Ground-glass plug.

II Silver Electrode:

A. Silver rod.
B. Glass tube.
C. Wax seal.

III Glass Electrode:

A. Special glass.
B. Small calomel half-cell.
C. Buffer solution.

groups of the side chains to coördinate silver ions.[13] This becomes less effective as the bromide-ion concentration is increased.

Carroll and Hubbard [14] had previously determined the relationship between pH and silver-ion concentration for certain emulsions, but it was necessary to make independent determinations for the emulsion which we used. This was a reproducible emulsion of fairly high speed, with only a small iodide content. As finished it had a pH of 7.60 and a pAg of 8.35. The procedure was as follows: A sample of emulsion was titrated with 0.1 *N* $AgNO_3$ solution, and the pAg measured after each addition, as well as the pH. The data are shown in Curve 2 of Fig. 3. A fresh sample of the emulsion was adjusted to a different (lower) original pH with 0.5 *N* $H_2SO_4$, and titration again made with 0.1 *N* $AgNO_3$ solution. The data are shown in Curve 3 of Fig. 3. Similarly, Curve 10 was obtained by first lowering the pAg with 0.1 *N* $AgNO_3$, then titrating with 0.5 *N* $H_2SO_4$, and measuring pH and pAg after each titration. The composite of graphs in Fig. 3 represents eleven separate titrations in which both pH and pAg were measured.

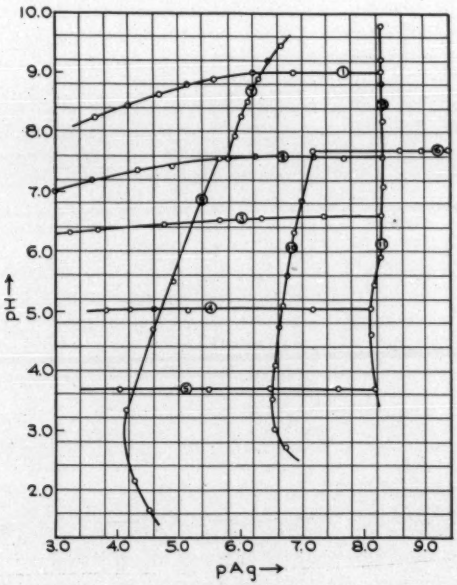
In comment on these, it may be noted that the greatest effect of change of pH and the pAg (vertical graphs) is found in the region of lowest pAg. When the number of silver ions about equals or exceeds the number of bromide ions, the silver-ion activity is greatly influenced by pH. When the bromide ions are in excess, the pH has little effect on pAg (at any rate between pH = 4 and pH = 10). It will be noted that on the vertical curves there is no noticeable inflection point at either pH = 7.0 or pH = 4.9, respectively, the acid base neutralization point, and the isoelectric point of gelatin.

The greatest effect of change of pAg on pH (horizontal graphs) is in the region of high pH and disappears at low pH. As stated, in order that the silver-ion concentration should influence pH, the former must exceed the bromide-ion concentration. In graphs 1, 2 and 3 there is a well-marked inflection point at pAg = 5.8, the equivalence point of silver and bromide ions.

The data are in general agreement with those presented by Carroll and Hubbard [14] and in the main features are probably

general for gelatino-silver bromide emulsions. For the immediate point of view of the present work, it is important to note that with this emulsion the pH could be altered between 5 and 10 without any significant change in pAg taking place. Conversely (Cf. graphs 2 and 6), the pAg could be altered between 6.0 and 9.0 without changing the pH.

FIG. 3.




Interrelation of pH and pAg in a gelatino-silver bromide system.

EFFECT OF pH AND MOISTURE CONTENT (RELATIVE HUMIDITY) ON SENSITIVITY AT CONSTANT pAg.

Observations on the effects of the relative humidity of the atmosphere (or the equilibrium moisture content of the gelatin) on photographic sensitivity have been made at different times but without very concordant results. Sheppard and

Wightman [9] found for a given emulsion that the sensitivity decreased considerably as the R. H. was raised from 50 to 100 per cent. (at ca. 25° C.) while Dimitroff [9] observed that an emulsion was faster at about 0 per cent. R. H. than at 100 per cent. In the following study the emulsion just discussed was employed, the pH being adjusted with 0.1 *N* NaOH or $H_2SO_4$ solution. Between pH = 7.5 and 9.5, a buffer solution was used to minimize pH changes by drying and absorption of carbon dioxide. Larger plates coated with given samples were cut into strips 35 mm. × 108 mm. for conditioning, exposure and processing. They were stored in a cabinet kept at constant temperature and humidity. The apparatus for combined humidity control (conditioning) and graded exposure to light (sensitometry) was a light-tight monel metal box, 36 × 24 × 18 inches, fitted with an intensity-scale sensitometer so that exposures could be made without removing the plates from the cabinet. Arm holes fitted with heavy rubber gloves made it possible to move the plates about in the cabinet without opening it.

The humidity in the cabinet was adjusted by the use of sulfuric acid solutions of different strengths.[15] Two liters of solution were used at a time with a total surface of 325 square inches. The atmospheric conditions were checked at certain points with a hygrometer. In the presence of undiluted sulfuric acid it was assumed to be 0 per cent. R. H.* A motor and fan circulated the air through large connected openings at the ends of the cabinet. As sensitometer, a step-wedge (intensity scale) was used, placed in contact with the plate (after conditioning) and illuminated with a 50-watt lamp controlled by a rheostat and a photronic cell. The bulb was at 90 cms. and three sheets of flashed opal glass in the light path near the bulb assured uniform illumination.

In operation, three plates for each set were conditioned about 66 hours before exposure. After exposure they were transferred to the constant value humidor for 36 hours in order to recondition all plates to near the same value for development, which was carried out for 5 minutes at 18° C. in DK-50. At the same time three "standard conditioned" plates of each set were exposed, etc., to check the exposure,

* It was probably somewhat higher.

development, etc. The characteristic (H. and D.) curves were averaged from three checks. The results are tabulated in Table I and shown graphically in Fig. 4.

TABLE I.

| Emulsion Number. | pH. | Relative Humidity. | Per Cent.* Moisture. | Fog. | Relative Speed. | Relative Speed—Fog. | Relative Gamma. |
|---|---|---|---|---|---|---|---|
| 22 | 9.80 | 0 | 2.8 | 0.13 | 730 | 590 | 1.11 |
| | | 15 | 12.6 | .13 | 840 | 680 | 1.05 |
| | | 34 | 17.2 | .13 | 720 | 580 | 1.18 |
| | | 55 | 21.9 | .14 | 555 | 450 | 1.25 |
| | | 80 | 28.6 | .17 | 465 | 375 | 1.26 |
| 23 | 8.55 | 0 | 2.8 | .11 | 610 | 525 | 1.14 |
| | | 15 | 12.3 | .11 | 745 | 620 | 1.08 |
| | | 34 | 16.8 | .11 | 655 | 565 | 1.21 |
| | | 55 | 21.5 | .11 | 510 | 435 | 1.24 |
| | | 80 | 28.0 | .11 | 430 | 365 | 1.11 |
| 21 | 7.35 | 0 | 2.6 | .11 | 520 | 460 | 1.21 |
| | | 15 | 12.1 | .08 | 610 | 545 | 1.14 |
| | | 34 | 16.4 | .11 | 590 | 510 | 1.22 |
| | | 55 | 21.2 | .11 | 470 | 400 | 1.26 |
| | | 80 | 27.6 | .11 | 405 | 345 | 1.22 |
| 24 | 6.20 | 0 | 2.5 | .06 | 415 | 380 | 1.26 |
| | | 15 | 11.7 | .06 | 510 | 465 | 1.21 |
| | | 34 | 15.9 | .06 | 435 | 405 | 1.31 |
| | | 55 | 20.8 | .06 | 400 | 370 | 1.31 |
| | | 80 | 27.1 | .06 | 355 | 320 | 1.29 |
| 25 | 5.05 | 0 | 2.3 | .07 | 235 | 220 | 1.43 |
| | | 15 | 11.4 | .07 | 320 | 295 | 1.28 |
| | | 34 | 15.2 | .06 | 285 | 260 | 1.42 |
| | | 55 | 20.1 | .05 | 230 | 215 | 1.42 |
| | | 80 | 26.3 | .07 | 225 | 205 | 1.44 |

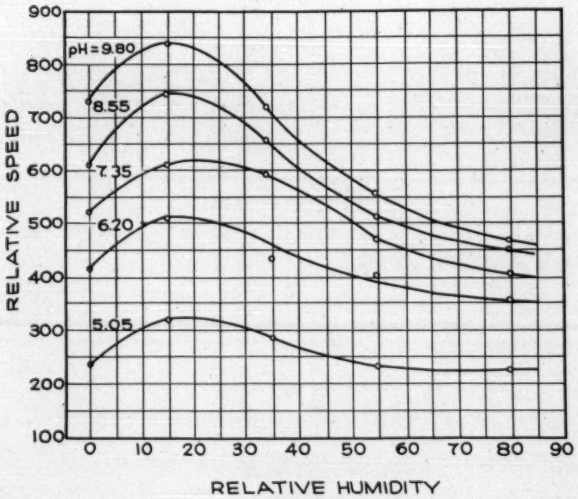
* Calculated in part from the data of Sheppard, Houck and Dittmar.

It will be seen that a maximum sensitivity is obtained at each pH at approximately 15 per cent. R. H.; at higher relative humidities, the sensitivity falls with increasing R. H., which agrees with the observations of Sheppard and Wightman. Also, there is not much difference in sensitivity between very dry plates, and those conditioned at ordinary R. H., e.g., 40 per cent. R. H. This may account for the observation of Cuffey,[10] who found no measurable difference between plates stored for three weeks over calcium chloride, and others which had received no special treatment. It is also apparent that

the absolute change of sensitivity with change of humidity is greater, the higher the pH of coating. Thus, at pH = 5.05, there is not much change of sensitivity with R. H., whereas at pH-9.8 the emulsion was twice as sensitive at 15 per cent. R. H. as at 80 per cent. R. H.

As the relative humidity is increased toward 100 per cent., the sensitivity difference due to the pH of the coating, i.e.,

FIG. 4.

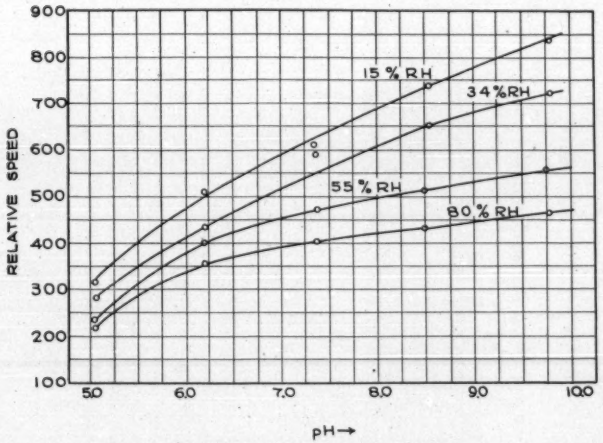



Relation of sensitivity to relative humidity at various pH values.

the reversible R. H. effect, becomes small. This is shown in Fig. 5, in which relative speed (sensitivity) is plotted against pH for differing R. H. values. This may account for the observations of Sheppard and Wightman [7] that, when an emulsion was soaked in aqueous solutions of differing pH, but exposed wet, the variation of sensitivity with pH was much narrower—not more than 1 : 2—than when the pH of a melted emulsion was adjusted before coating and the plates

exposed "dry." It may be noted that the *gamma* values for all emulsions were somewhat lower at the R. H. of highest speed—ca. 15 per cent.—but did not change significantly at higher humidities. Fog was unchanged between 0 and 80 per cent. R. H., except at the highest pH used, when the change was not considerable.

FIG. 5.




Relation of sensitivity to pH at various humidities.

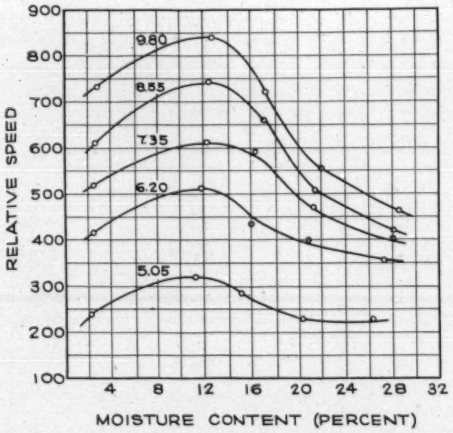
While for practical photography and for sensitometry, relative humidity is the more interesting variable, for latent-image formation it is the actual water content of the emulsion, or probably, better, of the gelatin. A study of the moisture sorption of gelatin as a function of pH, and other variables, has been made recently in these Laboratories by Sheppard, Houck and Dittmar.[11] Using the procedures indicated by them and, where necessary, their data, the present correlation of sensitivity with R. H. at different pH values can be expressed in terms of per cent. moisture content, as shown in Fig. 6.

It must be noted that in consequence of the sorption hysteresis of gelatin,[11] this correlation, and equivalently the correlation of:

i. Sensitivity with pH,
ii. Sensitivity with R. H.,
iii. Sensitivity with pAg,

can never be more precise than the hysteresis deviation at the R. H. in question.

FIG. 6.




Relation of sensitivity to moisture content of gelatin at various pH values.

**EFFECT OF pAg AND MOISTURE CONTENT (RELATIVE HUMIDITY) ON SENSITIVITY AT CONSTANT pH.**

The same basic emulsion was used as in the experiments with varied pH. It was employed at a pH of 7.45, at which it was sufficiently buffered. The pAg was altered by addition of 0.1 *N* $AgNO_3$ or KBr solution, the required amount, ascertained from an electrometric titration curve, being diluted to 10 cc. before addition to 250 cc. of emulsion. The conditioning and exposure were carried out in the cabinet already described and the experimental procedure was the same.

The results are given in Table II and in the graphs of Figs. 7 and 8.

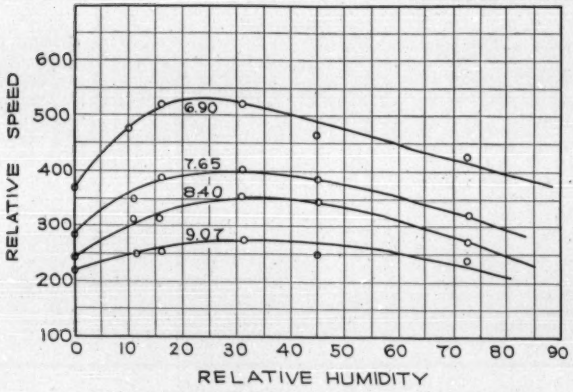
TABLE II.

| Emulsion Number. | pAg. | Run. | Relative Humidity. | Per Cent. Moisture Content. | Fog. | Relative Inertia Speed. | Relative Speed—Fog. | Gamma. |
|---|---|---|---|---|---|---|---|---|
| 56 | 9.07 | 1 | 0 | 2.8 | 0.13 | 218 | 183 | 1.44 |
| | | 2 | 11 | 10.3 | .13 | 246 | 204 | 1.51 |
| | | 3 | 16 | 13.3 | .12 | 251 | 209 | 1.56 |
| | | 4 | 31 | 15.4 | .13 | 275 | 228 | 1.54 |
| | | 5 | 45 | 18.9 | .12 | 251 | 209 | 1.60 |
| | | 6 | 77 | 26.4 | .13 | 237 | 192 | 1.42 |
| 57 | 8.40 | 1 | 0 | 2.5 | .14 | 240 | 195 | 1.45 |
| | | 2 | 11 | 10.7 | .14 | 310 | 246 | 1.46 |
| | | 3 | 16 | 13.5 | .14 | 312 | 248 | 1.48 |
| | | 4 | 31 | 15.7 | .14 | 353 | 276 | 1.50 |
| | | 5 | 45 | 19.1 | .15 | 346 | 274 | 1.44 |
| | | 6 | 77 | 26.7 | .14 | 275 | 222 | 1.43 |
| 58 | 7.65 | 1 | 0 | 2.5 | .15 | 280 | 215 | 1.49 |
| | | 2 | 11 | 11.1 | .15 | 343 | 265 | 1.47 |
| | | 3 | 16 | 13.7 | .15 | 385 | 305 | 1.42 |
| | | 4 | 31 | 15.7 | .15 | 400 | 315 | 1.50 |
| | | 5 | 45 | 18.5 | .14 | 385 | 305 | 1.43 |
| | | 6 | 77 | 26.7 | .15 | 325 | 255 | 1.42 |
| 59 | 6.90 | 1 | 0 | 2.5 | .18 | 365 | 275 | 1.46 |
| | | 2 | 11 | 10.5 | .17 | 475 | 365 | 1.44 |
| | | 3 | 16 | 13.3 | .18 | 520 | 385 | 1.47 |
| | | 4 | 31 | 15.4 | .17 | 520 | 400 | 1.49 |
| | | 5 | 45 | 18.2 | .18 | 470 | 355 | 1.44 |
| | | 6 | 77 | 29.2 | .19 | 430 | 320 | 1.45 |

The curves relating sensitivity to R. H. and moisture content are similar to those when the pH was varied, but the maximum is not so pronounced, and appears to occur at slightly higher values of R. H. or moisture content.

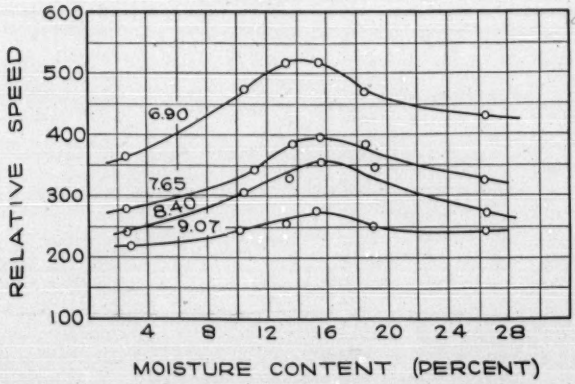
The data for variable pH were obtained for only one pAg, and those for variable pAg at only one pH. It is evident that with sufficient of these, a plot of sensitivity in terms of pH, pAg, and R. H. (or $H_2O$ content) as three orthogonal axes would give a *characteristic sensitivity* surface, representing a reversible or thermodynamic environment factor in photographic sensitivity. This factor is the extragranular factor, which is superimposed on the infragranular factors of crystal size, crystal (sub)-structure, and nucleation. It appears probable that the external or thermodynamic environment

FIG. 7.




Relation of sensitivity to relative humidity at various pAg values.

FIG. 8.




Relation of sensitivity to moisture content of gelatin at various pAg values.

factor must also be strongly temperature-dependent, and that consequently recent tendencies [4] to discuss the temperature influences on sensitivity exclusively in terms of infragranular processes must be incorrect to some at present unknown extent. It appears evident that a presumably secondary process in latent-image formation is occurring at the interface of the silver halide grain with the gelatin, which is controlled by the moisture content. The important new fact which the present investigation has brought out is that this humidity or moisture factor is intimately connected with the reversible pH and pAg—or more properly, pBr effects.

### NATURE OF THE SECONDARY PROCESS.

There is little doubt that the secondary extragranular process is concerned with the combination and removal of halogen (in the present case, bromine). The question arises as to the reaction or reactions concerned. It was suggested by Slater Price [8] in regard to the reversible pH (Rawling's) effect on sensitivity that this could be explained in terms of the kinetics of bromination of gelatin. The primary reaction of bromine with water gives the equilibrium

$$Br_2 + H_2O \rightleftharpoons HOBr + HBr,$$

which may be written

$$Br_2 + H^+ + OH^- \rightleftharpoons 2\,H^+ + OBr^- + Br^-,$$

whence

$$[OBr^-] = k\frac{[Br_2][OH^-]}{[H^+][Br^-]}.$$

Slater Price suggests various, supposedly reversible, reactions of halogen with gelatin as follows:

*a.* $Br_2 + \text{Gelatin} \rightleftharpoons \text{Gel Br} + Br^- + H^+$
*b.* $HOBr + \text{Gelatin} \rightleftharpoons \text{Gel Br} + H_2O$
*c.* $OBr^- + \text{Gelatin} \rightleftharpoons \text{Gel Br} + OH^-$

(or analogously for chlorine).

Qualitatively, the evidence is in favor of the view that the reaction between the hypobromite ion and gelatin is the one of principal importance, but reaction (*c*) above is probably an excessive simplification of what happens when halogen

reacts with gelatin. These reactions are under investigation and will be reported separately. In the meantime, assuming that the primary removal of bromine is effected through conversion to hypobromite (subsequently reacting with gelatin) as indicated above, then the reversible influences of pH, of pBr, and of moisture on sensitivity are qualitatively accountable. The influence of hydrogen ion (pH) and of bromide ion (pBr) are indicated by the hypobromite equilibrium. The behavior of moisture ($H_2O$) is as would be expected, since, at first, water is necessary for the hydrolysis of the bromine, but beyond a certain amount will simply act to dilute the active hypobromite.

Although the phenomena are satisfactorily accounted for, on the qualitative side, by consideration of gelatin as the halogen acceptor, there are alternative possibilities which must be considered. In a paper by Carroll and Hubbard,[14] discussing the influence of pH and pBr, they agree with Slater Price that these must be interpreted in terms of halogen acceptance. But they inclined to postulate another halogen acceptor than gelatin, viz., silver sulfide. "Admitting the existence of an efficient bromine absorbent in silver bromide-gelatin emulsions, we believe that consideration of all the evidence favors Hickman's hypothesis [16] that it is silver sulphide. It does not seem necessary to accept Hickman's further hypothesis that the reaction leads to increased liberation of metallic silver; it is sufficient if we assume that it merely prevents regression, since the quantum yield for the photolysis of silver bromide in photographic emulsions is more probably less than one, rather than greater than one. The silver sulphide is present in quantities of the right order of magnitude to correspond to the capacity observed. [This refers to the fact that extra halogen acceptors are required to stop solarization.] On the hypothesis that the silver sulphide nuclei orient [17] photolysis of silver bromide, they may become preferred bromine absorbents merely by virtue of position, and the orientation hypothesis may be retained even though the latent image is explained in terms of structure of photolytic silver [18] rather than quantity."

It appeared that an experimental investigation of the influence of pH on the relative ratio of attack of bromine on

silver sulfide, silver, and these two substances in the presence of gelatin, i.e., as photographic images, might afford, if not crucial, at any rate definite evidence on the question.

### RATE OF BROMINE WITH SILVER SULFIDE IMAGES IN GELATIN.

The silver sulfide images were prepared * by exposing "bromide" paper behind a step-tablet, developing, and converting the silver image to silver sulfide. After drying, strips of approximately equal dimensions were cut. Bromine solutions of varying pH were prepared by diluting equal volumes of the same (approximately) saturated bromine solution in water to ten volumes, and adding small amounts of concentrated sulfuric acid and sodium hydroxide solutions. The actual pH values were measured with a glass electrode.

The silver sulfide strips were immersed in these solutions and agitated vigorously during the reaction. At fixed intervals they were removed, rinsed, and fixed in thiosulfate ("hypo") solution. This stopped reaction by destroying all residual bromine and dissolving the silver bromide produced by the reaction, which otherwise darkened on exposure to light. The amount of bromine was made large in comparison with that consumed, so that its variation of concentration was not a significant factor, and this also eliminated the need of buffers for pH.

Typical results are illustrated in Fig. 9. In this case the time of reaction was 1.5 minutes. The relatively abrupt transition, within a short pH range, from almost complete bleaching of the image to nearly zero reaction is typical of all the results obtained but the locus of transition, referred to pH, depends on factors such as time, concentration of bromine, and depth of image.

### REACTION OF BROMINE WITH SILVER IMAGES IN GELATIN.

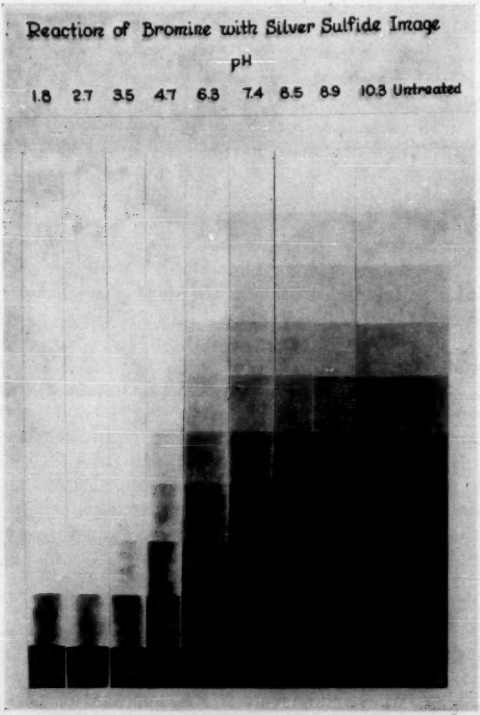
Similar experiments were performed with the unsulfided silver image on developed "bromide" paper. As will be seen from Fig. 10 the trend is much the same as for the silver sulfide image, there being again a rather abrupt intermediate region.

* Our thanks are due to Mr. S. M. Furnald of the Process Department for the preparation.

REACTION OF BROMINE WITH PRECIPITATED SILVER SULFIDE.

To investigate the reaction between bromine (in solution) and silver sulfide free from gelatin, an attempt was made at first to use pure filter paper having different amounts of silver

FIG. 9.

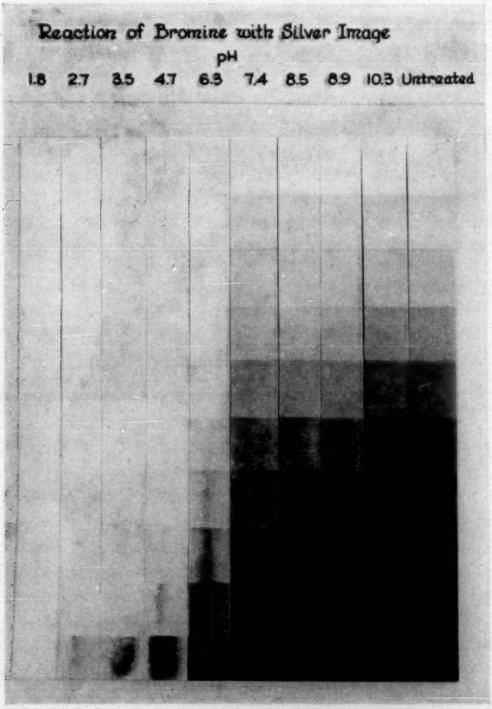



sulfide precipitated in it per unit area. However, very uncertain results were obtained, with changing pH, the latter factor, indeed, not appearing to influence the rate markedly.

Very possibly the distribution and packing of the sulfide varied more than was visually apparent.

Experiments with silver sulfide sols were also unsatisfactory, in that the reaction was very rapid and complicated

FIG. 10.




(photometrically) by the reaction product, silver bromide. We therefore had recourse to precipitated silver sulfide, following the reaction by titration of the bromine consumed.

The precipitate was prepared by the reaction between nearly equivalent amounts of silver nitrate and sodium sulfide solutions, with a slight excess of silver ion. The curdy precipitate was washed free of detectable silver ion, and shaken through silk bolting cloth under methyl alcohol to secure a uniform powder. This powder was then thoroughly dried.

Preliminary experiments in excess of bromine solution showed that the silver sulfide reacted with a small amount of bromine, then became practically inert. This is presumably due to the formation of a coating of silver bromide—as indicated by the fact that treatment at this stage with hypo solution followed by washing enabled reaction again to proceed. This necessitated using an excess of sulfide rather than an excess of bromine. In this case there is the liability of a large pH change during the reaction, because of the release of hydrogen ion on oxidation of the sulfide. The solutions were therefore buffered, with the following combinations:

*a*. Hydrochloric acid and potassium chloride,
*b*. Acetic acid and sodium acetate,
*c*. Monopotassium phosphate and sodium hydroxide,
*d*. Boric acid, potassium chloride, and sodium hydroxide.

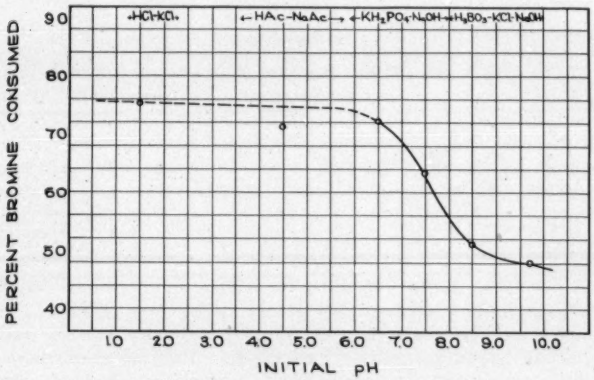
The base solutions were made 0.1 *N* with respect to the buffering ion; in the reaction mixture the concentration was 0.05 *N*, allowing for the buffering action of the bromine itself. A series of six steps was used ranging from pH = 1.5 to pH = 9.7. In the experiments, portions of the silver sulfide powder (0.2 grams) were shaken thoroughly with 50 cc. of buffer solution and 50 cc. of stock bromine water added—about 20 per cent. saturated. The flasks were kept vigorously agitated for 2 minutes. The mixture was quickly filtered, and 50 cc. of the filtrate treated with a solution of 1 gram of potassium iodide, and 5 cc. of 5.0 *N* hydrochloric acid in 50–60 cc. of water. After standing (in stoppered vessels), the iodine released by the unused bromine was titrated with thiosulfate. The pH of the remaining bromine solution was measured with a glass electrode. The results of two series of determinations (each the average of two) are given in Table III. They are also shown graphically in Fig. 11.

TABLE III.

*The Amount of Bromine Consumed at Various pH of the System.*

| Initial pH. | Final pH. | Per Cent. Bromine Consumed. | | |
|---|---|---|---|---|
| | | 1st Run. | 2nd Run. | Average. |
| 1.5 | 1.5 | 75.6 | 75.0 | 75.3 |
| 4.5 | 4.0 | 69.8 | 72.4 | 71.1 |
| 6.5 | 6.2 | 71.0 | 73.2 | 72.1 |
| 7.5 | 7.9 | 64.5 | 61.6 | 63.1 |
| 8.5 | 8.6 | 51.6 | 50.6 | 51.1 |
| 9.7 | 10.2 | 46.4 | 49.2 | 47.8 |

FIG. 11.




Reaction of bromine with silver sulfide in the presence of buffers.

It is believed that the value at pH = 4.5 is too low, the error being perhaps due to the acetate buffer.

The behavior of pure silver sulfide with bromine solutions is not what would at first be predicated if the reactions involved are as follows:

$$Ag_2S + 2\,OBr^- = 2\,AgBr + SO_2$$
$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$
$$H_2SO_3 + OBr^- = H_2SO_4 + Br^-.$$

It would seem on this view that the rate of reaction should

*increase* with pH, rather than decrease. However, there is an important factor which is not expressed in the above stoichiometric equations. This is the impedance to the reaction produced by the relatively insoluble layer of AgBr. Now, at low pH values, when the equilibrium

$$Br_2 + OH^- \rightleftharpoons OBr^- + Br^-$$

lies to the left, it is possible that free bromine may exert some solubilizing action on the AgBr layer, owing to the formation of $Br_3^-$ ions. Again, increase in the concentration of $OBr^-$ ion would increase the rate of removal of sulfite by oxidation to sulfate, whereby another solubilizing factor is diminished.

## CONCLUSIONS.

The attack of aqueous bromine solutions on silver sulfide is not favored but rather slowed down by raising the pH of the solution, whether the silver sulfide be free or incorporated in gelatin. This is evidence against the view that silver sulfide is the chief halogen acceptor in the photographic reaction. It is, therefore, more probable that it is gelatin, which, in this rôle, induces the specific behavior of the gelatino-silver halide emulsion in regard to pH, moisture, and pBr.

The rather limited capacity for halogen acceptance in such emulsions, as evidenced by solarization, was adduced by Carroll and Hubbard as an argument against this view and favoring the silver sulfide hypothesis. But, as they themselves point out, this argument is not cogent, because the effective halogen-accepting power of the gelatin would be limited to the small amounts adsorbed to the silver halide grain, and which need to be supplemented by *diffusible* halogen acceptors to prevent solarization.

ROCHESTER, N. Y.,
JUNE 28, 1940.

## REFERENCES.

1. Cf. S. E. SHEPPARD, *Ber. VIII Internat. Kongr. Phot.* (Dresden), p. 13, 1931.
2. S. E. SHEPPARD AND W. VANSELOW, *J. Phys. Chem.*, **33**, 331, 1403 (1929).
3. R. W. GURNEY AND N. F. MOTT, *Proc. Roy. Soc.*, **A-164**, 151 (1938).
4. J. H. WEBB AND C. H. EVANS, *J. Opt. Soc. Amer.*, **28**, 249 (1938).

5. J. H. WEBB AND C. H. EVANS, *loc. cit.*
W. F. BERG, *Trans. Farad. Soc.*, **35**, 445 (1939); *Proc. Roy. Soc.*, **A-174**, 559 (1940).
6. S. O. RAWLING, *Phot. J.*, **67**, 42 (1927).
S. O. RAWLING AND J. W. GLASSETT, *Phot. J.*, **66**, 495 (1926).
7. S. E. SHEPPARD AND E. P. WIGHTMAN, *Phot. J.*, **69**, 134 (1929).
8. T. SLATER PRICE, *Phot. J.*, **71**, 59 (1931).
9. S. E. SHEPPARD AND E. P. WIGHTMAN, *Ber. VIII Internat. Kongr. Phot.* (Dresden), p. 157, 1931.
10. G. Z. DIMITROFF, *Harvard College Observatory Circular*, No. 430.
J. CUFFEY, *Bull. Harvard College Observatory*, **905**, 12 (1937).
11. S. E. SHEPPARD, R. C. HOUCK AND C. DITTMAR, *J. Phys. Chem.*, **44**, 185 (1940).
12. S. E. SHEPPARD, W. VANSELOW AND G. P. HAPP, *J. Phys. Chem.*, **44**, 411 (1940).
13. B. H. CARROLL AND D. HUBBARD, *Bur. Stand. J. Res.*, **7**, 811 (1931).
S. E. SHEPPARD, *J. Soc. Mot. Pict. Eng.*, **24**, 500 (1935).
14. B. H. CARROLL AND D. HUBBARD, *Bur. Stand. J. Res.*, **8**, 481 (1932).
15. R. E. WILSON, *Ind. Eng. Chem.*, **13**, 326 (1921).
16. K. C. D. HICKMAN, *Phot. J.*, **67**, 34 (1927).
17. S. E. SHEPPARD, *Phot. J.*, **68**, 397 (1928).
18. Cf. (1) *loc. cit.*; also S. E. SHEPPARD, *Phot. J.*, **71**, 313 (1931).

**The New York Air Brake Company.**—On July 1, 1940, The New York Air Brake Company was fifty years old. During its span of life and that of its predecessor, the Eames Vacuum Brake Company, men have learned to control with safety the movement of railroad trains. Without that control, built up through the years of experiment and experience, the science of modern transportation as we know it would not have been possible. Abraham Lincoln rode on railroad trains the safety of which depended upon the anticipation and muscle power of brakemen turning hand brakes on car platforms. Until 1880, railroad men scarcely considered the possibility of applying automatic brakes to freight cars. Yet today one is safer on a railroad train than in his own home. The story of air brakes and what they do has been obscured in the emphasis placed upon speed and equipment design in recent years, but were it not for advances in the art of air braking, the present day 100 mile per hour passenger schedules and 150 car freight trains would not be actualities on the country's railroads. A beautiful brochure published in commemoration of the fiftieth anniversary of the New York Air Brake Company sketches in some detail the development through the years. Few of the passengers whose safety is maintained by air brakes or shippers whose goods are delivered without damage realize how complex and yet how reliable an air brake is. The intricate mechanism of the brake is manufactured under conditions of great precision, for the combined capacity of brakes on a train often represents 15 to 20 times the tractive power of the locomotive. The successive actuation of brakes on cars as the compressed air flowed through the pipe from the engineer's control valve was slow in the early stages of brake development. Now it is so fast that it approaches the speed of sound, and on some modern passenger trains brakes are actuated instantaneously from the engineer's cab by electrical transmission. Brake design has had to shorten progressively the retardation cycle in relation to the work to be done, otherwise the enormous gain in railroad locomotive power and train momentum would have prolonged that cycle intolerably.

R. H. O.

# BACTERICIDAL IRRADIATION OF AIR.

NOTE BY

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W. F. Wells gave in his paper published in the March issue of this JOURNAL [1] the following formula for the number of live bacteria $N(t)$ in a sphere of radius $R$ after a time $t$ of exposure to a lethal radiation if the radiation source is at the center of the sphere and the bacteria are fixed in the space:

$$N(t) = \frac{3N_0}{R^3}\int_0^R r^2 e^{-ct/r^2}\cdot dr. \tag{1}$$

$N_0$ is here the initial number of live bacteria and $c$ is a positive constant depending on the vulnerability of the organisms and on the bactericidal power of the radiation source.

If the bacteria flow in a infinite circular cylinder of radius $R$ with a constant velocity $v$ parallel to the cylinder axis directed from $-\infty$ to $+\infty$ and if the radiation source is at a point of the axis, the relation between the number of live bacteria per unit length of the cylinder at $-\infty$ and at $+\infty$ is, according to another formula of Wells:

$$\frac{n_{+\infty}}{n_{-\infty}} = \frac{2}{R^2}\int_0^R y e^{-\pi c/vy}\cdot dy. \tag{2}$$

The purpose of this short article is to show that the integrals in (1) and (2) may be calculated by means of the error integral

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}\cdot dx$$

and of the exponential integral

$$Ei(-x) = -\int_x^\infty \frac{e^{-x}}{x}\cdot dx.$$

[1] W. F. Wells, "Bactericidal Irradiation of Air," JOUR. FRANK. INST., 229, 347–372, 1940.

Applying then the known expansions in series of $\Phi(x)$ and of $Ei(-x)$,[2] approximate formulas for (1) and (2) are deduced similar to those which Wells obtained by empirical interpolation.

Put for brevity $a = ct$. The substitution of $x = \sqrt{a}/r$ in (1) and integration twice by parts gives, if one takes into account that $\Phi(\infty) = 1$:

$$(3)\quad N(t)/N_0 = (1 - 2aR^{-2})e^{-a/R^2} + 2aR^{-3}\sqrt{\pi a}[1 - \Phi(\sqrt{a}/R)].$$

Introducing here the first three terms of the expansion:[2]

$$\sqrt{\pi}[1 - \Phi(x)] = \frac{e^{-x^2}}{x}\left(1 - \frac{1}{2x^2} + \frac{3}{4x^4} - \frac{15}{8x^6} + \cdots\right),$$

we obtain for sufficiently large values of $a$ (e.g. of $t$ because $a = ct$):

$$(4)\quad \frac{N(t)}{N_0} \approx \frac{3}{2}\frac{R^2}{a}e^{-a/R^2}.$$

The corresponding approximate formula of Wells is: $N(t)/N_0 = e^{-1.28a/R^2}$, which for $\sqrt{a}/R = 2.3231$ gives $N(t)/N_0 = 0.001$, whereas the exact value calculated by means of (3) using the tables of the error integral $\Phi(x)$ [2] is: $N/N_0 = 0.0009465$. The approximate formula (4) gives here $N/N_0 = 0.00126$.

In formula (2) put for brevity $b = \pi c/v$. The substitution $y = b/x$ and integration twice by parts gives then:

$$(5)\quad n_{+\infty}/n_{-\infty} = (1 - bR^{-1})e^{-b/R} - b^2R^{-2}\cdot Ei(-b/R).$$

Introducing here the first three terms of the expansion:[2]

$$Ei(x) = \frac{e^x}{x}\left(1 + \frac{1}{x} + \frac{2}{x^2} + \cdots\right),$$

we obtain if $b/R \gg 1$:

$$(6)\quad n_{+\infty}/n_{-\infty} \approx 2(R/b)e^{-b/R}.$$

The corresponding formula of Wells is:

$$(7)\quad n_{+\infty}/n_{-\infty} \approx e^{-1.24b/R}.$$

[2] See for instance E. Jahnke and F. Emde, "Tables of Functions," Leipzig, 1933, 2nd ed., pp. 78–80, 83–85, 98.

If $b/R = 5.5708$, (7) gives $n_{+\infty}/n_{-\infty} = 0.001$, whereas the exact value is by (5) 0.0009223.[3] Formula (6) gives here: 0.001367.

## DISCUSSION.

BY

DR. WILLIAM FIRTH WELLS.

I am much indebted to Dr. Opatowski and Dr. Smith * for rigorous solution of the two integrals expressed in my paper on "The Bactericidal Irradiation of Air." They remove the stigma of incompleteness which Dr. Swann held in view of available techniques to be mathematically inexcusable, and I must confess that the beautifully simple approximations derived by Dr. Opatowski deprive me of the excuse that medical men who face death objectively recoil subjectively from the horrors of infinite series. Admiration for the mathematical elegance of these rigorous solutions or the nice simplicity of the mathematical approximations need not blind us to the fact that they apply only to theoretical situations. Since actual conditions involve a mixing factor, both accuracy and simplicity demand empirical determination of a coefficient in practice. Nevertheless, the solutions contribute to a better understanding of the mathematical conditions essential to study of the theory of irradiation of microörganisms suspended in air.

[3] This value has been calculated using the tables of $Ei(x)$ of the Brit. Ass. Adv. Sc., "Mathematical Tables," vol. I, London, 1931.

* Smith, J. F. Downie, "The Killing of Bacteria with Ultra-violet Light," J. FRANKLIN INST., 229, 775, 1940.

**Research—New Products—New Jobs.**—(*Mill and Factory*, Vol. XXVII, No. 1.) Fifteen million Americans now work at jobs which did not exist in 1900, said Everett S. Lee, head of the General Electric general engineering laboratory at Schenectady, in an address on the "Practical Applications of Research" at Providence, R. I., at a dinner of executives celebrating "Research Day in New England." "These jobs exist today," said Mr. Lee, "because through research, industry has been able to develop hundreds of new products. And it has been able to make them so inexpensive that millions of people have been able to buy them." He said that there are now 1700 distinct research groups in America, employing some 50,000 workers and spending 150 to 200 million dollars a year, but that there is still room for more research. In 1938, he said, more than 150,000 manufacturing concerns were without research laboratories.

R. H. O.

**Tacoma Bridge Oscillations Being Studied by Model.**—(*Engineering News Record*, Vol. 125, No. 5.) The University of Washington engineering department at Seattle has undertaken a study of the vertical oscillation of the deck of the Tacoma Narrows suspension bridge, seeking to discover means of reducing the movements, which were observed even before completion of the structure and have given the engineers much concern. They are believed to result from wind action. Measurements show that the bridge floor rises and falls over a maximum range of $2\frac{3}{4}$ ft.; very little side sway has occurred. According to L. V. Murrow, Washington state highway engineer, under whose direction the bridge was built, the safety of the structure is not affected. However, some persons are reported to have become seasick because of the oscillation. Motion pictures show an up-and-down movement similar to gentle waves on water, readily seen from either shore. Experiments are to be conducted on a scale model of the bridge, which has been equipped with devices to cause the model to simulate this rippling action, and damping devices of various kinds will be tried out. The Tacoma bridge is the narrowest long-span suspension bridge ever built; the cables are only 39 ft. apart and the roadway is 24 ft. wide, though the main span of the bridge is 2,800 ft. long, third largest in the world.

R. H. O.

## NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

### SOLAR ECLIPSE.

The total eclipse of the sun on October 1, 1940, was observed from a point near the village of Patos, Brazil, by an expedition sponsored by the National Geographic Society and the Bureau. Dr. Irvine C. Gardner, chief of the Optical Instruments Section, is the leader of the party, which is made up of Dr. Paul A. McNally, S. J., Director of Georgetown Observatory; Dr. E. O. Hulbert, of the Naval Research Laboratory; Dr. Carl C. Kiess, of the Bureau's Spectroscopy Section; Theodore R. Gilliland, of the Radio Section; and Richard H. Stewart, staff photographer, National Geographic Society.

The site selected for the eclipse camp is on the center line of the path, and since the sun will have an altitude of approximately 54°, and totality will last for nearly 5 minutes, an unusually favorable opportunity is presented. Moreover, the location is a high plateau and the season is normally dry.

The equipment includes the astrographic camera designed and built at the Bureau in 1936 (*Technical News Bulletin* 236 (December, 1936)), two small, compact corona cameras, and two special spectrographs, each capable of photographing a portion of the sun's spectrum 40 inches long. These spectrographs are slitless, using concave gratings and no lenses. The focal length is about 11 feet, and as the film magazines are mounted on a slant, the photographs overlap without interfering. In other words, only 12 inches of film, 9 inches wide, need be wound between exposures, although each picture is 40 inches long. In the two instruments, the sun's spectrum is divided, so that one takes care of wave-lengths from 3,000 to 5,500 A., and the other from 5,000 to 10,000 A. The gratings were prepared with extreme care to produce unusually bright images. One has 15,000 lines per inch, ruled by Robert A. Wood of Johns Hopkins, and the other,

* Communicated by the Director.

by Henry G. Gale of the University of Chicago, has 30,000 lines per inch.

All the eclipse instruments are tied together by a combined electric and vacuum control system which makes the operation of the numerous units almost completely automatic. As the result of many rehearsals, the program has been worked out in detail. A roll of paper, somewhat like a player piano roll, punched with the necessary holes and slots, is run through the "program clock" at a definite speed. Through the open spaces, electrical contacts are made which open and close shutters, wind films, and apply suction to hold the films in their proper planes. A recorder operated by a chronometer makes a record of all operations, measuring exposures to a fraction of a second. This record will be of the greatest value in developing the films and in a study of brightness from the photographs.

The radio measuring equipment which will record the height of the ionized layers before, during and after the eclipse, is not connected with the electric control system, but is operated independently. The instruments are all installed in an automobile trailer, this field laboratory having been successfully used in studying ionosphere phenomena during the annular eclipse of April 7, 1940 (*Technical News Bulletin* 278 (June, 1940)).

The program is expected to include: A complete motion picture record in color of the eclipse; photographs of the "flash spectrum"; repeated photographs of the spectra of the corona; special large photographs of the corona, in black-and-white and in color, with different exposures; records of the polarization of the coronal light; measurements of ionosphere phenomena; studies of sky brightness, radiation, and spectra; and records of temperature and density changes in the atmosphere. Times of contact may also be recorded.

The expedition, which left the United States on August 24, will sail from Recife on October 14, and should reach New York about October 23.

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**PORTABLE BRIGHTNESS METER FOR LUMINOUS PREPARATIONS.**

A compact portable photometer for measuring the brightness of the luminous paints used on clocks, watches, and air-

plane instruments has been constructed from the design of Leon F. Curtiss, chief of the Bureau's Radioactivity Section. An arrangement of stainless steel mirrors is used to bring the light from the luminous paint into view adjacent to a luminous pattern from a reference lamp, the brightness of which can be controlled and calibrated. These mirrors do not tarnish and therefore require no protective coating which might cause undesirable reflections and also deteriorate with age. Since comparisons are made at fixed positions from the luminous paint and the reference lamp the instrument is very compact and rigid. Therefore, it is not easily put out of adjustment by rough handling.

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### EFFECTS OF COBALT AND NICKEL IN STORAGE BATTERIES.

As a part of a more general investigation of methods for decreasing the evolution of hydrogen from storage batteries, G. W. Vinal, D. N. Craig, and C. L. Snyder have made experiments on the change in charging potentials when small amounts of cobalt and nickel are added to the electrolyte. Hydrogen evolution, as a result of local action within the cell, is generally attributed to antimony derived from the positive plates and deposited on the negative plates. Reduction in the charging potentials of positive plates should decrease corrosion of the positive grids and therefore diminish the quantity of antimony which can be deposited on the negatives.

Because of the related properties of the elements, cobalt and nickel, to iron, experiments with all three were made in commercial types of batteries subjected to 150 cycles of charge and discharge. Single potentials of the positive and negative plates were measured and compared with those of other cells to which no additions had been made.

As reported in RP1335 in the October *Journal of Research*, the presence of cobalt decreases the charging potentials of positive plates, nickel decreases the potential of the negative plates, but iron has little if any effect on the potential of either positives or negatives. The advantages that might accrue from the use of cobalt are offset by its destructive action on the separators. If this can be avoided, the lower charging voltages should be advantageous and some of the

substitutes that have been proposed for lead-antimony alloys may find increased use in storage batteries.

## MOISTURE CONDITIONS IN CONCRETE.

The moisture condition of concrete is intimately connected with its volume changes, the hydration of the cement, and the life of paint or linoleum applied to the surface. A method for determining this moisture condition has been developed by G. R. Gause and John Tucker, Jr., and is described in the October *Journal of Research* (RP1334). An electric hygrometer, devised by F. W. Dunmore and previously described in this *Bulletin*, measures the relative humidity inside a cavity within the concrete.

The relative humidity inside 12-inch concrete cubes stored at relative humidities of 50 and 20 per cent. was measured over a period of 10 months. The humidity inside uncoated specimens ranged as follows:

| Time of Storage. | Relative Humidity. | Location of Hygrometer. | |
|---|---|---|---|
| | | 1½ In. Deep Hole. | 6 In. Deep Hole. |
| Days. | Per Cent. | | |
| 50 | 50 | 70 | 92 |
| 300 | 50 | 50 | 66 |
| 50 | 20 | 52 | 90 |
| 300 | 20 | 20 | 60 |

The relative humidity inside hermetically sealed specimens was found to decrease as the temperature decreased, and the change appeared to be completely reversible. Neat cement pastes of approximately normal consistency were cured in hermetically sealed bottles and the relative humidity over the pastes was measured. The relative humidity over a moderate heat of hardening cement was 94 per cent. at 7 days and 88 per cent. at 28 days' age. Over a high early strength cement the relative humidity was 88 per cent. at 3 days, 82 per cent. at 7 days, and 79 per cent. at 28 days' age. The electric hygrometer was found to be well suited to the measurement of relative humidity inside concrete and over cement pastes.

### EFFECTIVENESS OF CEILING INSULATION.

The effectiveness of various types of insulation in preventing high ceiling temperatures under a flat roof in a test structure was determined experimentally under summer conditions in Washington, D. C. The results are presented in Building Materials and Structures Report BMS52, in tabular and graphical forms. Ceiling temperatures with insulation above the ceiling were as much as 16° F. lower than the temperatures of uninsulated ceilings. With only an attic floor in place, ceiling temperatures were about 10° lower than on the uninsulated ceiling. The various types of insulation tested were very nearly equal in effectiveness.

Copies of this report are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 10 cents each.

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### DRYING OF TEXTILE YARNS.

The combined effects of heat and moisture on the properties of yarns made from the common textile fibers were studied in the course of recent work at the Bureau by the research associateship of the United States Institute for Textile Research. The results may be considered basic to all types of textile drying according to a paper (RP1337) by James G. Wiegerink in the October *Journal of Research*.

Yarns made from raw cotton, "purified" cotton, mercerized cotton, clothing wool, carpet wool, viscose rayon, cuprammonium rayon, cellulose acetate, and degummed silk were saturated with water and then exposed for periods of from ½ to 6 hours in air having temperatures of 221°, 257°, and 302° F., and absolute humidities of approximately 1, 55, and 95 per cent. After conditioning the dried yarns for at least 24 hours in air of 65 per cent. relative humidity and 70° F., measurements were made of: The breaking strengths, elongations at break, and moisture contents of the yarns; the fluidities of dispersions of the cellulosic fibers in cuprammonium solution, of the silk in aqueous zinc chloride, and of the acetate in aqueous acetone; and the relative affinities of the cellulosic fibers for the dye Benxopurpurine 4B and of the wools for acid dyes.

Heating for 6 hours at 221° F. and each of the three humidities weakened all of the yarns. The breaking strength and elongation at break of the viscose, cuprammonium, degummed silk, and cotton yarns decreased still more at higher temperatures. In comparison with heating at 1 per cent. absolute humidity, heating at 95 per cent. absolute humidity resulted in lower breaking strengths and elongations at break for all yarns except the raw cotton, higher fluidities, lower affinity of cellulosic fibers, and higher affinity of wool fibers for the dyes.

Heating for ½ hour at 302° F. had little effect on the properties of the yarns, except the viscose and cuprammonium rayon, which were adversely affected. The damage which occurred at a given temperature and humidity increased throughout the heating period.

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### EFFECT OF SOOT ON RATING OF HEATING BOILERS.

If heating boilers or furnaces are tested and rated on a basis of constant flue gas temperature, due care should be taken to assure that soot, deposited on the heating surfaces, does not interfere with the process. A light layer of soot, one thirty-second of an inch thick or less, can materially influence the relation between flue gas temperature and boiler output.

In ordinary service an increase in flue gas temperature due to soot is not necessarily accompanied by a proportionate or serious decrease in efficiency.

Designers of chimneys, especially those interested in prefabricated chimneys, should remember that soot, deposited by oil burner maladjustment or otherwise, may cause flue gas temperatures to be sufficiently high to damage or destroy chimney liners or flues designed only for moderate or low temperatures. The implication is that chimneys designed for heating devices, which can, under any conditions, deposit soot, should be capable of withstanding high temperatures, equal to or approaching flame temperatures. These conclusions are based on tests at the National Bureau of Standards which are described in detail in Building and Materials Structures Report BMS54 which has just been issued.

As part of the program on materials and equipment for low-cost houses, the Bureau undertook to study methods of rating heating boilers. At about the same time the Institute of Boiler and Radiator Manufacturers proposed a set of codes, one of which covers oil-burning boilers. Trials under this code were conducted in the Bureau's laboratories and effects attributable to soot were soon noted. Because this has an important bearing on operating results, the tests reported in BMS54 were undertaken.

In these tests the boiler was operated under "stand-by" conditions for a number of days and the capacity efficiency, etc., were determined once each day at the constant stack temperature of 600° F. One of the two runs was made with 10 per cent. carbon dioxide in the flue gas and the other with 8 per cent. At the end of each run the soot was cleaned out and the boiler was found to operate as at the beginning, indicating that certain effects observed during the run were attributable to the soot.

When the flue gas temperature was maintained constant by adjusting the firing rate while the boiler was operating under "stand-by" conditions, the soot considerably diminished the boiler capacity. Likewise, the flue gas temperature was materially increased by the soot if the firing rate or the output of the boiler were kept constant.

Copies of BMS54 are obtainable from the Superintendent of Documents, Government Printing Office, at 10 cents each.

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### TIMEKEEPING THROUGH THE AGES.

Each year the Bureau receives many inquiries from school children and others concerning the devices used by peoples of ancient times down to the present era to mark the passing of time. To meet the demand for this information, Letter Circular LC600, Timekeeping through the Ages, has been prepared by Katharine S. Vandoren in which the subject is presented in an easily read and interesting manner.

Single copies of LC600 will be sent free on requests addressed to the Bureau.

**Scientists Find Six Periodic Fluctuations in Sun Constant.**—(*Heating and Ventilating*, Vol. 37, No. 8.) At least six periodic fluctuations in the so-called solar constant, all of which are included in a ten-year period, have just been reported to the National Academy of Sciences by a group of Harvard University mathematicians after an intensive analysis of observations made over an interval of 15 years by Smithsonian Institution observers. The solar constant is the amount of solar radiation—heat, light, and ultra-violet radiation—which would be absorbed each minute by a black cube one cubic centimeter in size placed at the outer edge of the earth's atmosphere. It is essentially the amount of solar radiation which would fall on a square centimeter of the earth's surface if the planet, like its satellite the moon, had no atmosphere. This solar constant is approximately 1.940 calories. If the heat output of the sun was constant, this figure would never fluctuate. For several decades, however, there has been accumulating evidence gathered by Smithsonian observers that it does fluctuate, that these fluctuations are rhythmic, and that consequently the sun must be a variable star. The Harvard investigations were made entirely without reference to any of the previous findings. Altogether they found ten solar variation cycles. Six of these upon which chief emphasis is placed are almost exact submultiples of 10.2 years. This is highly suggestive of the sun-spot cycle, during which the number of titanic cyclones in the atmosphere of the sun goes from a minimum to a maximum and back again. The length of the sun-spot cycle is generally considered to be approximately 11.3 years. This is close to the average since observations were started. The period, however, varies in length, and it so happens that the two sun-spot periods, parts of which fell within the 15-year sample period for which the records were analyzed, averaged 10.1 years. Thus the six fluctuations would seem to be components of the major sun-spot cycle itself—due fundamentally to the same unknown causes.

R. H. O.

# THE FRANKLIN INSTITUTE.

## STATED MONTHLY MEETING, OCTOBER 16, 1940.

The regular monthly meeting of The Franklin Institute was called to order at 8:15 o'clock by Mr. W. Chattin Wetherill, Vice-President.

The minutes of the May meeting were approved as printed in the June issue of the Journal.

The Secretary announced that the additions to membership since last report were as follows:

| | |
|---|---|
| Active | 26 |
| Associate | 18 |
| Student | 49 |
| Total | 93 |

The Chairman then introduced the speaker of the evening, the Honorable Lewis Compton, Assistant Secretary of the Navy, who addressed the meeting on "Naval Policies and Developments since the World War." *

The speaker devoted his attention largely to the research and development program which he felt contributed most to the navy's present state of high efficiency. He referred to the building program which was initiated in 1916 and which was suspended after the Disarmament Conference of 1922. It was not until 1929 that Congress finally recognized the fact that other powers were promoting a building race in everything except battleships and that we were lagging behind. Fifteen cruisers and one aircraft carrier were thereupon authorized but this program was suspended in the following year. He referred to the interest which the late Thomas A. Edison displayed especially in the Naval Research Laboratory which was finally established in 1923. He outlined briefly the present naval program for the defense of the western hemisphere.

Adjourned,

HENRY BUTLER ALLEN,
*Secretary.*

# LIBRARY NOTES.

The committee on Library desires to add to the collections of the Institute any technical writings of members who have had occasion to publish such material.

Literary contributions from author-members will be gratefully acknowledged, properly inscribed and noted in the Journal of the Institute.

Photostat Service. Photostat prints of any material in the collections can be supplied on request. Orders received in the morning are filled the same day. The average cost for a print $8\frac{1}{2} \times 11$ inches is forty cents.

The library and reading room are open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays two until ten o'clock P.M. 637 readers made use of the facilities during the twenty-five days of September.

* To appear in full in the next issue of the Journal.

## RECENT ADDITIONS.

### AERONAUTICS.

LAW, BERNARD A. Fighting Planes of the World. 1940.
TURNER, ROSCOE, AND JEAN H. DUBUQUE. Win your Wings. 1940.

### AGRICULTURE.

Association of Official Agricultural Chemists. Official and Tentative Methods of Analysis. Fifth Edition. 1940.

### ASTRONOMY.

MERRILL, PAUL W. Spectra of Long-Period Variable Stars. 1940.

### BIBLIOGRAPHY.

MELLON, M. G. Chemical Publications. Second Edition. 1940.

### CHEMISTRY AND CHEMICAL TECHNOLOGY.

BINNS, CHARLES F., Editor. The Manual of Practical Potting. Fifth Edition. 1922.
BOURRY, EMILE. Treatise on Ceramic Industries. Revised Translation—by Alfred B. Searle. Fourth Edition. 1926.
CAROTHERS, WALLACE HUME. Collected Papers on High Polymeric Substances. 1940.
GLASSTONE, SAMUEL. Text-Book of Physical Chemistry, 1940.
HODGMAN, CHARLES D., Editor. Handbook of Chemistry and Physics. Twenty-fourth Edition. 1940.
KEANE, CHARLES A., AND P. C. L. THORNE, Editors. Lunge and Keane's Technical Methods of Chemical Analysis. Second Edition. Volume 4. 1940.
KELSEY, ERWIN B., AND HAROLD G. DIETRICH. Fundamentals of Semimicro Qualitative Analysis. 1940.
MCCORMACK, HARRY, Editor. The Applications of Chemical Engineering. 1940.
MALINOVZSKY, A. Ceramics. 1921.
MUDD, J. S. Leather Finishes. 1939.
RADLEY, J. A. Starch and Its Derivatives. 1940.
RICE, OSCAR KNEFLER. Electronic Structure and Chemical Binding. 1940.
SEITZ, FREDERICK. The Modern Theory of Solids. First Edition. 1940.
WARING, RALPH G. Wood Finishing and Painting Made Easy. 1940.
WIGNER, J. H. Soap Manufacture. 1940.

### DICTIONARIES.

DEVRIES, LOUIS. French-English Science Dictionary. First Edition. 1940.

### EDUCATION.

College Blue Book. Fourth Edition. 1939.

### ELECTRICITY AND ELECTRICAL ENGINEERING.

DUNLAP, ORRIN E. The Story of Radio. 1935.
Electrochemical Society. Transactions. Volume 77. 1940.

GRAY, ALEXANDER. Principles and Practice of Electrical Engineering. Fifth Edition. 1940.

MANTELL, C. L. Industrial Electrochemistry. Second Edition. 1940.

Massachusetts Institute of Technology. Members of the Staff of the Department of Electrical Engineering. Electric Circuits. 1940.

MOSELEY, SYDNEY A., AND H. J. BARTON-CHAPPLE. Television To-Day and To-Morrow. Fifth Edition. 1940.

RIDER, JOHN F. FM: An Introduction to Frequency Modulation. 1940.

### ENGINEERING.

ACKERMAN, ADOLPH J., AND CHARLES H. LOCHER. Construction Planning and Plant. First Edition. 1940.

Great Britain. War Office. Overstrain of Metals and its Application to the Auto-Frettage Process of Cylinder and Gun Construction, by Major A. E. Macrae. 1930.

TIMOSHENKO, S. Theory of Plates and Shells. First Edition. 1940.

### GEOLOGY AND GEOPHYSICS.

MABY, J. CECIL, AND T. BEDFORD FRANKLIN. The Physics of the Divining Rod. 1939.

NETTLETON, L. L. Geophysical Prospecting for Oil. First Edition. 1940.

### MATHEMATICS.

HOGBEN, LANCELOT. Mathematics for the Million. New, Revised and Enlarged Edition. 1940.

KASNER, EDWARD, AND JAMES NEWMAN. Mathematics and the Imagination. 1940.

PLUMMER, H. C. Probability and Frequency. 1940.

UNDERWOOD, RALPH S., AND FRED W. SPARKS. Living Mathematics. First Edition. 1940.

### MECHANICAL ENGINEERING.

FRENCH, THOMAS E., AND CARL L. SVENSEN. Mechanical Drawing. Fourth Edition. 1940.

LONGSTREET, J. R., AND W. K. BAILEY. Turret Lathe Operator's Manual. 1940.

MONCHER, SAMUEL C. Commercial Refrigeration and Comfort Cooling. 1940.

### METEOROLOGY.

PETTERSSEN, SVERRE. Weather Analysis and Forecasting. First Edition. 1940.

### MINING ENGINEERING.

American Institute of Mining and Metallurgical Engineers. Transactions. Coal Division. 1940.

RICHARDS, ROBERT H., AND CHARLES E. LOCKE. Assisted by Reinhardt Schuhmann. Textbook of Ore Dressing. Third Edition. 1940.

### NAVAL ARCHITECTURE AND NAVIGATION.

MARRAN, RAY J. Making Models of Famous Ships. 1940.

### PHARMACY.

British Pharmacopoeia 1932. Second Addendum. 1940.

### PHOTOGRAPHY.

Modern Photography 1940–41.

### PHYSICS.

BIRREN, FABER. Color Dimensions. 1934.
BIRREN, FABER. Functional Color. 1937.
EDDINGTON, SIR ARTHUR. The Philosophy of Physical Science. 1939.
FREEMAN, IRA M. Invitation to Experiment. 1940.
MARKS, PERCY L. Acoustics. 1940.
MAYER, JOSEPH EDWARD, AND MARIA GOEPPERT MAYER. Statistical Mechanics. 1940.
TIMOSHENKO, S., AND D. H. YOUNG. Engineering Mechanics. Second Edition. 1940.
VENNARD, JOHN K. Elementary Fluid Mechanics. 1940.

### SANITARY ENGINEERING.

IMHOFF, KARL, AND GORDON MASKEW FAIR. Sewage Treatment. 1940.
TURNEAURE, F. E., AND H. L. RUSSELL. Public Water Supplies. Fourth Edition, Revised. 1940.

### SCIENTIFIC ESSAYS.

HALDANE, J. B. S. Science and Everyday Life. 1940.

### TECHNOLOGY—HISTORY.

BURLINGAME, ROGER. Engines of Democracy. 1940.
HATFIELD, H. STAFFORD. Inventions and their Uses in Science Today. 1940.
Newcomen Society for the Study of the History of Engineering and Technology. Transactions 1938–1939. Volume 19. 1940.

## NOTES FROM THE BARTOL RESEARCH FOUNDATION.

### THE LATITUDE EFFECT IN COSMIC RAYS AT FAR SOUTHERN LATITUDES.*

BY

E. T. CLARKE AND S. A. KORFF.

Two meters for measuring the total cosmic-ray intensity from all directions, namely a single Geiger counter [1] and an electroscope of the type described by Millikan and Neher,[2] were operated on board the *U.S.S. North Star* during a recent trip through the Antarctic regions. The electroscope was operated on the Philadelphia-Panama-Dunedin, New Zealand-Little America run, while the counter set was operated on that from Dunedin to Little America-Valparaiso-Palmer Land-Valparaiso-Panama. The electroscope was inside a 10-cm. thick lead shield, and the single Geiger counter was inside 7.5 cm. of lead. The counter counts, approximately 190,000 per day, were scaled down with a conventional thyratron scale-of-four circuit [3] and then recorded on a dial recorder. The daily mean counting rate and the daily mean electroscope reading were corrected for changes in atmospheric pressure by applying the same barometer coefficient to each. The daily mean counting rate was then multiplied by an arbitrary constant to enable it to be shown on the same scale as the electroscope ionization. The corrected readings were then plotted against geomagnetic latitude and are presented in Fig. 1.

It will be observed that the cosmic-ray intensity shows the familiar "knee" at approximately geomagnetic latitude 38° south. Between the knee and 77° south the intensity rises by $3 \pm 0.3$ per cent., this rise being shown by both the

* Reprinted from the *Physical Review*, **58**, 179 (1940).

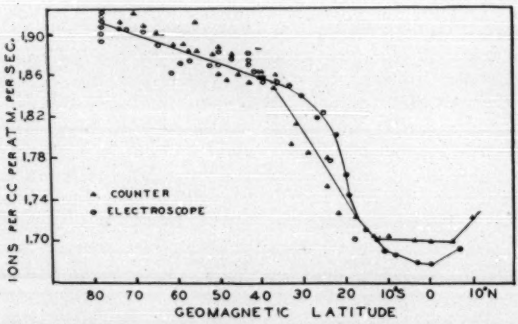
[1] E. T. Clarke and S. A. Korff, *Phys. Rev.*, **58**, p. 201A.

[2] R. A. Millikan and H. V. Neher, *Phys. Rev.*, **50**, 15 (1936).

[3] C. E. Wynn-Williams, *Proc. Roy. Soc.*, **A136**, 312 (1932).

counter and the electroscope. At latitudes nearer the equator the curves obtained by the two meters are not exactly similar, since the above routes carried the two instruments through quite different longitudes and hence through different horizontal magnetic intensities at corresponding geomagnetic latitudes. The electroscope readings, taken at longitudes farther west than the counter observations, are lower at the equator. The application of an external temperature coefficient of $-0.15$ per cent. per degree C. to the data will cause

FIG. 1.




Cosmic-ray intensities as measured by electroscope and counter, in southern latitudes. The differences between the curves in middle latitudes is due to longitude effect. Each point is a daily mean. The electroscope remained on board the ship at 72° S. for six days before being put ashore, and the normal daily fluctuations may be judged from the corresponding six points. The data are not corrected for external temperature.

the intensity curve to become horizontal between the knee and 77° south, the highest geomagnetic latitude reached. This may be compared with a coefficient of $-0.18$ found by Compton.[4] These observations were made during January and March, the summer months in the Southern Hemisphere; at this season it is to be expected, from the observations of Hess,[5] that the temperature coefficient will be at a minimum.

It will be noted that the counter and electroscope measurements show the same increase with latitude above the knee.

[4] A. H. Compton and R. N. Turner, *Phys. Rev.*, **52**, 799 (1937).
[5] V. F. Hess, *Phys. Rev.*, **57**, 781 (1940).

Since the counter counts the total number of rays, while the electroscope measures the total ionization, it is evident that the average specific ionization per ray at sea level remains constant with change in latitude above the knee. From this it can be shown that the ratio of electrons to mesotrons is constant.

The results will be discussed in detail in a forthcoming issue of the JOURNAL OF THE FRANKLIN INSTITUTE.

We wish to acknowledge the support of the Carnegie Institution of Washington in connection with the use of the Millikan-Neher meters, as well as film for these donated by the Eastman Kodak Company and batteries presented by the Burgess Battery Company.

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## THE SECONDARY PEAK IN THE ROSSI CURVE FOR TIN.*

BY

W. F. G. SWANN AND W. E. RAMSEY.

The apparatus, already described [1] comprised primarily five separate horizontal counter areas each containing 18 counters 20 cm. long and giving a sensitive area (analyzing tray) 20 cm. by 20 cm. The areas were arranged in a vertical array and tin was inserted between the top tray (the first) and the next tray (the second). One-centimeter slabs of lead were placed over trays 3, 4 and 5 for subsidiary reasons. Each counter was connected to an individual electroscope. In addition, above the second tray, but below the tin, there was another counter tray (master tray), without electroscopes. The arrangements were such that the electroscopes were only allowed to operate when at least one ray passed through the whole apparatus including the master tray which, by a side lead shield, guarded against electron showers from the side. The electroscopes recorded photographically the shower history of every *event* associated with the passage of a ray through the whole apparatus.

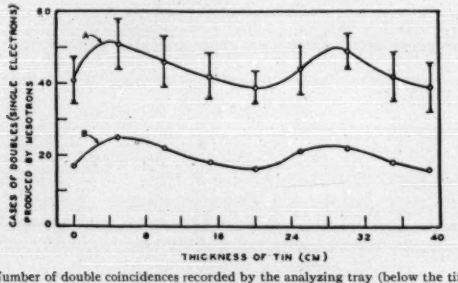
Figure 1 curve *A*, shows, plotted against thickness of tin, the number of doubles recorded by the second analyzing

* Reported from the *Physical Review*, **58**, 477 (1940).

tray (below the tin) per 1000 events. It will be observed that the curve shows two maxima, the second one being at 29 cm.

Each point for curve *A* corresponds in actuality to 1000 observations of events except in the case of the points for 20 cm. and 30 cm., which correspond to 2000 observations each. The standard deviations are indicated by the vertical lines. At first sight it is surprising that their magnitude permits the degree of regularity exhibited by the curve. The statistics of this matter will be discussed in greater detail in a more complete publication later to be presented. For the present, it will perhaps cement confidence in the reality

FIG. 1.



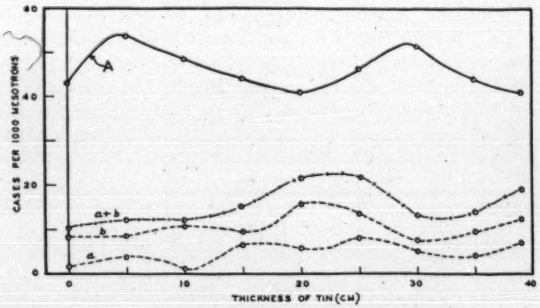

Number of double coincidences recorded by the analyzing tray (below the tin) as a function of the thickness of the tin.

of the minimum at 20 cm. in the case of curve *A* by replotting, as in Fig. 1, curve *B*, the results obtained by utilizing, for each point, just half of the observations utilized in drawing curve *A*. The statistical errors for curve *B* are, of course, considerably greater, proportionally, than for curve *A*. However, the minimum is still well marked. It may be added that in order to avoid systematic changes with time, the curve *A* was not obtained by taking all the observations for the individual points in succession. A smaller number of observations was taken for the whole set of points and repeated backwards and forwards so as to ensure that as far as possible the observations for each point extended over the same period of operation of the apparatus.

It was found that, in 75 per cent. of the cases, at least one member of each of the two-ray showers disappeared in the lead plate above the third analyzing tray, thus guaranteeing that the shower electrons were in the relatively low energy class.

Figure 2 indicates, in addition to curve $A$ corresponding to Fig. 1, the curve $a$ for quadruple rays, curve $b$ for triple rays,

FIG. 2.




Curve $A$, number of double coincidences; curve $a$, number of quadruple coincidences; curve $b$, number of triple coincidences as function of the thickness of tin.

and $a + b$ for the sum of triples and quadruples. In these cases all the curves have been corrected for inefficiency of counter trays, which correction is more important in the case of large showers. Of course, the statistical errors in the large showers are very large, but it is interesting to note that the minimum for doubles is approximately compensated as regards total number of showers by the triples and quadruples.

[1] W. F. G. Swann, *Rev. Mod. Phys.*, 11, 242 (1939).

## NOTES FROM THE BIOCHEMICAL RESEARCH FOUNDATION.

**The Molecular Basis of Resin Behavior.**—E. O. KRAEMER. (Condensation of paper presented at Gibson Island Conference on Organic High Molecular Weight Compounds, June 8, 1940. (Continued from page 518.))

*Non-Uniformity of Molecular Size.* With the exception of some crystallizable proteins and certain synthetic polymers prepared by quite special methods (for instance Hibbert's polyoxyethylene glycols) all soluble macromolecular materials are mixtures, and the complete definition of molecular weight requires the use of a size-distribution curve. Non-uniformity is most readily demonstrated by fractional dissolution or precipitation and comparison of the properties of the fractions. Clean-cut separation of the different molecular species is of course not possible, and a reasonably accurate size-distribution curve requires repeated fractionations. Spurlin probably holds the record for extensive fractionation with his separation of a low-viscosity nitrocellulose into 67 fractions. Schulz has published size-distribution curves for polystyrenes involving 10–12 fractions, using them to confirm theoretically calculated distributions derived from the kinetic analysis of the process of polymerization and condensation (see papers by Flory, Mark, Schulz and others).

The most generally applicable direct method for determining heterogeneity is by means of the sedimentation equilibrium with the ultracentrifuge. Unfortunately, it does not give a detailed representation of the heterogeneity, but rather an equivalent heterogeneity which may be expressed in terms of a suitable empirical distribution function. Consideration of the interpretation of the sedimentation equilibrium of mixtures led to a method of characterizing heterogeneity in terms of what we called weight-average and Z-average molecular weights, both of which can be calculated from the ultracentrifuge data, provided all molecular species have the same V-value and light absorption or refractive increment at some

usable wave-length. The latter average is always larger than the former, and the relative difference is larger the more heterogeneous the sample. In a chapter discussing this matter in "The Ultracentrifuge" by Svedberg and Pedersen, the author gives a suitable distribution equation for defining a numerical non-uniformity coefficient in terms of the ratio of weight- and Z-average molecular weights, and values at present available for various macromolecules are summarized. Flory and Schulz have shown that ideal polymerization should lead to a degree of heterogeneity represented by a value of two for the ratio of the number- and weight-average molecular weights, corresponding to a non-uniformity coefficient of 1.2. This represents a mixture extending over a range of 1 to 25 in relative molecular weight.

For molecules which are roughly spherical (axial ratio not over 5–10) and not too small (i.e., with a sufficiently low diffusion coefficient) detailed size-distribution curves can be obtained from sedimentation velocity in the ultracentrifuge. If diffusion is appreciable, then one must be satisfied with an equivalent heterogeneity, as in the case of sedimentation equilibrium. For highly elongated molecules, such as are characteristic of the macromolecules of industrial importance, it is difficult to carry out ultracentrifugal analysis at concentrations sufficiently low to permit unhindered separation of the molecules of different size. In addition, one must know the relation between sedimentation velocity and molecular weight (i.e., the friction factor) before a distribution curve can be calculated. Because of these difficulties, only one size-distribution curve by sedimentation velocity for a polymer of high intrinsic viscosity has so far been published, namely Signer's curve for polystyrene. This curve does not agree with the size-distribution inferred from sedimentation equilibrium, probably owing to the fact that the sedimentation velocity experiment was made at too high a concentration.

In theory, one may determine a non-uniformity coefficient from suitable diffusion measurements (e.g., by the Lamm method), and theoretically one can detect heterogeneity by the shapes of the curves relating internal friction or streaming birefringence to velocity gradient. Under favorable conditions dielectric dispersion may also reveal heterogeneity.

However, no definitive results are available for any of these possibilities.

*Evidence for Molecular Solutions.* In general, physical methods for molecular weight really give the size of the kinetic unit, and other evidence is required in order to distinguish between single molecules and aggregates. The evidence is apt to be of a circumstantial character, but in view of the different types of evidence available, there is now good reason to believe that soluble macromolecules commonly disperse to single molecules in suitable active solvents at very low concentrations. In support of this conclusion, evidence along the following lines can be offered:

1. The homogeneity of molecular weight, as for many proteins.
2. The constancy of molecular weight in different solvents.
3. The relative constancy of intrinsic viscosity in different solvents, although it seems that the intrinsic viscosity in different solvents may differ appreciably even though the molecular weight does not.
4. The constancy of molecular weight at different temperatures.
5. The small temperature coefficient of intrinsic viscosity, say 0.9–0.95 per 10°C.
6. Polymer-analog conversions, as carried out by Staudinger and my co-workers.

Perhaps the most convincing evidence for molecular solutions is provided by item 6, by which is meant the agreement in the calculated stoichiometric inter-relationships between the molecular weights of related macromolecules having the same skeleton and differing only in the nature of substituent groups, for instance of cellulose, cellulose acetate, cellulose nitrate, ethyl cellulose, etc. If such materials can be converted into each other without degradation, and the solutions are molecular, the relative values of the molecular weights can be calculated from the known chemical composition of the materials. Frankly, it is often difficult to obtain perfect proof for molecular solutions by these means, but at least some of the discrepancies are due to the great difficulty in completely preventing degradation during polymer conversions and to uncertainties in the extrapolation of experimental

molecular weight data to zero concentration. Departures from ideal behavior may also arise from differences in molecular coiling or solvation in different solvents or at different temperatures. In higher concentrations, which by ordinary standards may still be very low, association undoubtedly sometimes occurs, but it is not possible at present to estimate the degree of association in any rational manner.

*Shapes of Macromolecules in Solution.* A good deal of attention has been given in the last few years to the question of the form of macromolecules, particularly with respect to the flexibility and degree of coiling of the linear type of molecule, and the correlation of shape and viscosity. The results have been encouraging, but so far not very conclusive. For an infinitely thin chain of equal segments having completely free rotation around each joint, it is comparatively easy to calculate the probability for all possible distances between the two ends of the chain, when the chain is completely isolated. However, there is good reason to believe that the rotation about even a normal paraffin chain is very much restricted, and the restrictions must become more marked for substituted paraffin chains or chains of rings, as in cellulose derivatives, even ignoring specific attractive forces between adjacent chains along the chain. When in addition, the chain molecule is solvated, as it must be in solution, restrictions become still greater, so as Frenkel argues, many linear molecules which on first sight might be expected to be much coiled up in solution, may well be substantially straight. This is also Staudinger's point of view. If this is admitted, the problem then arises as to the interpretation of Staudinger's viscosity law. For particles large enough to obey the laws of hydrodynamics, it is certain that the intrinsic viscosity would increase approximately as the square of the length of rod-like molecules. On the other hand, it seems doubtful that many linear molecules are thick enough, with respect to the size of the solvent molecules, to justify the application of hydrodynamics. This is the position of Signer and of Staudinger, in defense of their argument that linear molecules are substantially straight. An additional argument of considerable force is the fact that the constants of proportionality relating intrinsic viscosity and molecular length are so nearly constant for different

molecules, which would be expected to coil to different degrees owing to differences in the restrictions to free rotation. It is difficult to calculate satisfactorily the intrinsic viscosity to be expected from a coiled molecule because of the necessity of setting the coiled molecule equivalent to an ellipsoid (which is therefore partially filled with an unknown amount of solvent) or of assuming that the flow of solvent around adjacent groups in the chain is not affected by the presence of the adjacent groups. If the latter is true, then flow must occur through the ellipsoid assumed in the former method of calculation. However, the latter assumption can scarcely be true because of the marked effect on viscosity of moderate concentrations of even spherical-particle suspensions.

The most extensive information regarding macromolecular shapes has been obtained from friction factors measured by means of diffusion or sedimentation velocity. The friction factor for a rigid sphere large in comparison to the dimensions of the molecules of the solvent is given by Stokes' equation and equals $6\pi\eta r$. According to methods worked out by Svedberg and his colleagues (see "The Ultracentrifuge" by Svedberg and Pedersen) the frictional ratio $f/f_0$, representing the ratio of the experimental friction factor to the factor for a spherical molecule of the same volume, can be calculated from the molecular weight and the diffusion constant or the sedimentation constant. If the molecule in question is spherical, unsolvated, and without electrical charge (or the effects of charge are neutralized by an excess of neutral salt), it is evident that the $f/f_0$ value is unity. If the shape is nonspherical or the volume is increased by combination of the macromolecule with other components of the solution, $f/f_0$ is greater than one, but it is at present impossible to determine in an unambiguous manner to what extent shape or combination (usually solvation) is responsible for the departure from unity. Only for large values of the frictional ratio (e.g., over 2) is it possible to demonstrate that solvation alone could not be the cause for the high value by showing that the sedimentation velocity in a suitable mixed solvent would thereby be reversed in sign. (For the details of the argument, see a recent paper, now in press, by the author on gelatin and notes in this journal (JOUR. FRANK. INST., **228**: 531, 680, 1940).)

There is a close relationship between frictional ratio and intrinsic viscosity. For geometrically-simple shapes, the frictional ratio may be calculated, in principle, from viscosity data, assuming the applicability of hydrodynamic laws, but such calculations have hitherto been limited to rods and ellipsoids (see, for instance, recent papers by Simha). The volumetric intrinsic viscosity of spheres is equal to 0.025, and as the frictional ratio increases above 1.0, the ratio of the intrinsic viscosity to that for spheres increases approximately as the cube of the frictional ratio for elongated ellipsoids.

Experimental values for the frictional ratio for many proteins have been found in the range 1.0 to 1.5, and the intrinsic viscosities of these proteins are correspondingly low. For the high viscosity types of macromolecules, as cellulosic materials, synthetic vinyl polymers, rubber, and the like, the frictional ratio varies in the range 2 to 8 or 10. The degree to which these data are consistent with viscosity behavior and the calculations involving equivalent ellipsoids and corresponding equivalent axial ratios are illustrated in detail by the author and Nichols in "The Ultracentrifuge."

A powerful method for the investigation of the flexibility of macromolecules is provided by the thermodynamic treatment of solutions with regard to the free energies and entropies for swelling and dilution. However, with a polemic situation still existing between Schulz and Meyer, and taking into consideration the experimental difficulties in making the required measurements with satisfactory accuracy, it is not clear what the conclusions of this attack will be. Since this problem falls within the scope of Professor Mark's paper, it will be left to him to cover the matter in a more detailed manner.

Surveying the whole subject, we must admit that a good deal has been learned concerning the physical characteristics of macromolecules, although, on the other hand, only a good beginning has been made. A large number of experimental technics have been found, in what might be called preliminary investigations, to be effective in the study of macromolecules, but most of them still stand in need of further refinement and much more extensive application to the many types of macromolecules now available.

**Glycolic Acid Oxidase.**—JANETTA SCHOONOVER DOHAN (*Journal of Biological Chemistry*, **135**: 793, 1940). An enzyme which promotes oxygen consumption by glycolic acid has been found in washed minces of rat and rabbit livers. The reaction was carried out at 38° in phosphate buffer at pH 7.4, but there was an indication that the pH optimum was higher. All other tissues of the rat or rabbit which were tested were found to be inactive.

The major reaction was found to be the consumption of ½ mole of oxygen by 1 mole of glycolic acid. The rate of oxygen uptake was independent of the substrate concentration and directly proportional to the enzyme concentration within the limits tested.

The oxidase was discovered during a critical survey of the Cohen (*Biochem. J.*, **33**: 551, 1939) method for the determination of glutamic acid. In this method glutamic acid is converted to succinic acid and the succinate estimated by its oxygen uptake in the presence of heart succinoxidase. It was found that serine interfered if rat liver, instead of heart, was used as a source of succinoxidase. This was due, probably, to the formation of glycolic acid from the serine.

**The Effect of Alpha-Estradiol Benzoate on the Skeletal Development of Immature Rats.**—J. O. ELY AND R. LLOYD PHILLIPS (*Endocrinology*, **27**: 661, Oct. 1940). The administration of large amounts of estrogenic hormones to female mice and to immature female rats has been reported to produce hypermineralization of the bones of the skeleton. In producing such skeletal changes rats were treated with comparatively large amounts of the hormone from the day of birth to about ten days of age. In producing the changes in mice large amounts of the hormone have been administered over long periods of time. The limits of the amount of the hormone which may be administered without producing such changes have not been clearly defined.

The administration of estrogenic hormones to immature female rats produces an enlargement of the uterus and an involution of the thymus.

Work performed in this laboratory yielded results showing that a 198 per cent. increase in the size of the uterus and a 46.5

per cent. involution of the thymus could be produced in young female rats of the Douredoure strain by the administration of alpha-estradiol benzoate without producing demonstrable effects on the skeletal development as shown by ash determinations of the bones or Röntgenograms of the forepaws. The amount of estradiol benzoate administered varied from three doses totaling 50 gamma to fifteen doses totaling 250 gamma. The experimental periods varied from seven days to fifty days, the initial age of the animals from six to eighteen days, and the initial weights from eight to nineteen grams. The treatment produced no apparent effect on the growth of the animals as shown by the weights and by body length measurements.

**Studies on Capsule Formation. III. Inhibition of Capsule Formation of Klebsiella pneumoniæ (Friedländer's bacterium) by an Agent Produced by a Soil Bacillus.**—J. C. HOOGERHEIDE (*Journal of Bacteriology*, **39**: 415, 1940). While engaged in attempts to isolate from bacterial sources possible enzymes capable of hydrolysing the capsular polysaccharides of Friedländer's bacterium, several strains of a soil baccillus were isolated. This spore-forming micro-organism, when allowed to grow on different media (synthetic as well as peptone-broth) excretes an agent in the medium, by means of which this bacillus is able to prevent Friedländer's bacterium from forming capsules.

This soil bacillus could be isolated from many soil samples from different locations around Philadelphia. Traces of the sample as an inoculum in a synthetic medium with $NH_3$ as nitrogen source and Type B Friedländer's polysaccharide as the source of carbon were used to isolate the bacillus.

The bacillus which also grows abundantly on the usual nutrient media was obtained in pure culture by the plate technique. When growing in ordinary broth an agent is excreted making this broth a powerful inhibitory solution, small amounts of which when added to fresh broth prevented Friedländer's bacterium from forming capsules, whereas the growth of this organism was not impaired.

The agent responsible for this inhibition of encapsulation was isolated in a crude state from the supernatant fluid of a

broth culture of this soil bacillus by adding $(NH_4)_2SO_4$, redissolving the scum and then dialyzing the solution. A similar cell-free solution was prepared from the centrifuged and washed bacteria by sonic vibration of a bacterial suspension. The active principle is heat stable, is readily adsorbed on Norit or colloidal iron and does not pass a Seitz filter or a dialyzing membrane.

The inhibitory principle prevents the formation of the capsular poylsaccharide, but does not destroy it once it is formed.

## BOOK REVIEWS.

ELECTRONIC STRUCTURE AND CHEMICAL BINDING, WITH SPECIAL REFERENCE TO INORGANIC CHEMISTRY, by Oscar Knefler Rice. First Edition, 511 pages, illustrations, tables, 16 × 24 cms. New York, McGraw-Hill Book Company, Inc., 1940. Price $5.00.

Although this book was the outgrowth of a course of lectures entitled "Advanced Inorganic Chemistry," given by the author at Harvard, it bears little resemblance to the usual text on Inorganic Chemistry. The book, in the words of the author, ". . . has become essentially a discussion of the chemical bond as exemplified in inorganic compounds."

The object of the first part of the book is to give the reader an insight into the properties of electrons and atoms. This is done by means of an abridged quantum mechanical treatment, in which the author gives the ideas lying behind the theories, rather than all the mathematical detail.

This discussion moves logically into the consideration of theories of valence, and then various types of chemical bonds. A large portion of the book is devoted to study of types of binding in crystals. The last chapter considers water, hydrates, and aqueous solutions.

Although the emphasis in the book is largely on the side of inorganic chemistry, it is nevertheless required reading for the organic chemist.

The book is well written and well printed, and represents a good job very well done.

G. S. GARDNER

PRINCIPLES OF ELECTRICAL ENGINEERING SERIES. ELECTRIC CIRCUITS, A FIRST COURSE IN CIRCUIT ANALYSIS FOR ELECTRICAL ENGINEERS, by Members of the Staff of the Department of Electrical Engineering, Massachusetts Institute of Technology. 782 pages, illustrations, 16 × 24 cms. New York, John Wiley & Sons, Inc. Price $7.50.

Evidences of technological development in electrical engineering are plainly seen everywhere. Acceleration of applications is also very apparent. There is seldom any question raised beyond the mere acceptance of these facts. Yet, aside from the basic reason—the urge to greater accomplishment—human mechanics angle must of necessity be considered as a very large contribution to increasingly rapid development. More men with advanced knowledge are engaged in the work, there is more efficient coördination of activities and thought, and most important of all there has been a constant and progressive evolution in the methods of imparting knowledge to the workers. Without these, it is doubtful that progress could have been made on such a broad front.

This book is an illustration of progress sought and accomplished in teaching methods at the Massachusetts Institute of Technology. Dr. Karl T. Compton states, in the foreword, that the Department of Electrical Engineering has for some years been engaged in an extensive program of revising as a unit substantially its entire presentation of the basic technological principles of electrical engineering.

The result is a series of textbooks representative of a new synthesis of educational material and having a breadth of view not easily approached by an author working individually. Electric Circuits is the first book of this series.

The work requires a thorough grounding in direct and alternating currents as well as the principles of electrical machinery with attendant mathematical background including the calculus. It begins with the derivation and evaluation of circuit parameters in which there is developed the conception of two terminal electric circuit elements, or lumped parameters. This leads to a discussion of the simple fixed-resistance networks in which fixed voltages are applied, and the consideration of the solution of equations starting with very simple circuits. It is noteworthy that emphasis is laid on the general principles by which lumped parameter circuits are analyzed rather than only on the solutions, because once the principles are clearly understood, their application to more complicated networks is relatively easy though often laborious mathematically.

Steady state alternating current theory is next taken up. It is concerned with the response of the same constant parameter circuits to energy sources whose voltages or currents vary sinusoidally with time. A brief treatment of transient analysis of simple alternating current circuits intervenes before steady state analysis involving two unknowns is given attention, then transient analysis of the same. With regard to multibranch alternating current networks advanced methods of analysis are explained and under the heading of Loci of Complex Functions the investigation of characteristics of circuits having one parameter which varies according to known restrictions are related to methods of analysis.

An important special application of the general theory of linear alternating current networks to circuits whose voltage sources are inter-related in both magnitude and phase angle is developed which is most useful to the electric power engineer and there is presented the underlying theory of the method of symmetrical components. The last two chapters of the book are devoted to electromechanically coupled systems and transients in nonlinear circuits.

Being the product of a number of individuals with the idea in view of covering that which is of fundamental importance to all branches of electrical engineering, this book provides a presentation that is carefully weighed and measured to meet the basic needs of the qualified student. The subject index enhances its value as a means of reference.

The idea of integrating the subjects of a course such as this to the end of unity in purpose, as laid out by a series of texts of which this is the first, should be of interest to many educators particularly in engineering. It has been done with considerable success in other fields.

R. H. OPPERMANN.

CHEMICAL ENGINEERING CATALOG, 1940. Twenty-fifth Annual Edition. The Process Industries' Own Catalog. 1097 pages, quarto. New York, Reinhold Publishing Corporation.

After twenty-five years the Chemical Catalog has become the reference book of all who have any interest in chemistry and the chemical industries.

The present issue contains all the useful information and data which has appeared in previous years corrected to date. The scientific and technical books section contains titles of works published during the current year.

R.

## PUBLICATIONS RECEIVED.

*Scattering of Light and the Raman Effect*, by S. Bhagavantam. 333 pages, illustrations, 19 × 26 cms. Waltair, Andhra University.

*Geomagnetism*, by Sydney Chapman and Julius Bartels. Volume I, Geomagnetic and Related Phenomena. Volume II, Analysis and Physical Interpretation of the Phenomena. 2 volumes, 1049 pages, plates, illustrations, 17 × 25 cms. New York, Oxford University Press, 1940. Price $18.00.

*Copying Technique*, by Frank R. Fraprie and Robert H. Morris. 128 pages, illustrations, 16 × 24 cms. Boston, American Photographic Publishing Co., 1940. Price $1.50.

*Technical Drawing*, by Frederick Giesecke, Alva Mitchell and Henry Cecil Spencer. Second Edition, 687 pages, illustrations, plates, 16×24 cms. New York, The Macmillan Company, 1940. Price $3.00.

*Working Stresses*, by Joseph Marin. 41 pages, illustrations, 14 × 22 cms. New Brunswick, Rutgers University Press, 1940. Price $1.00.

*Physical Chemistry, A Brief Course with Laboratory Experiments*, by Louis L. Bircher. 429 pages, illustrations, 16 × 24 cms. New York, Prentice-Hall, Inc., 1940. Price $3.00.

*Foundations of Modern Physics*, by Thomas B. Brown. 333 pages, illustrations, 16 × 24 cms. New York, John Wiley & Sons, Inc., 1940. Price $3.25.

*College Physics*, by John A. Eldridge. Second Edition, 702 pages, illustrations, 15 × 22 cms. New York, John Wiley & Sons, Inc., 1940. Price $3.75.

*National Advisory Committee for Aeronautics*. Twenty-Fifth Annual Report, 1939. Including Technical Reports Nos. 645 to 680. 745 pages, illustrations, 24 × 30 cms. Washington, Government Printing Office, 1940. Price $2.50.

*Bell Telephone System*, Monographs: B-1239, Feedback Amplifier Design, by H. W. Bode. 34 pages, illustrations. B-1240, Crosstalk between Coaxial Conductors in Cable, by R. P. Booth and T. M. Odarenko. 27 pages, illustrations. B-1242, Crosstalk in Coaxial Cables, by K. E. Gould. 17 pages, illustrations. B-1243, Compressed Powdered Molybdenum Permalloy, by V. E. Legg and F. J. Given. 22 pages, illustrations. B-1244, High Accuracy Heterodyne Oscillators, by T. Slonczewski. 14 pages, illustrations. 5 pamphlets, 15 × 23 cms. New York, Bell Laboratories, 1940.

## CURRENT TOPICS.

**Farm Population Increased.**—On January 1, 1940, there were 32,245,000 persons living on farms, the Bureau of Agricultural Economics estimates. This figure is close to the all-time high record of 1916 when the farm population was 32,530,000 persons. The estimated increase for 1939 was 186,000. The analysis of farm population issued by the bureau in July says: In general, in the area best adapted to commercial farming there was enough migration away from farms in the last decade to have brought about a reduction in farm population, but in areas less well adapted to commercial farming there were increases.

R. H. O.

**Peoria Laboratory to Begin Immediate Study of Alcohol as Motor Fuel.**—One of the first studies of the new regional laboratory of the U. S. Department of Agriculture at Peoria, Illinois, will be the industrial uses of corn including the production of alcohol, stated the Secretary of Agriculture recently. Special attention will be given to the probable use of corn products in the national defense program such as the production of synthetic rubber, plastics and substitute fibers. A complete pilot plant for the production of alcohol from corn is being installed so that a full study may be made of the technical difficulties involved as well as its probable cost. Data gathered by Department scientists indicate that an arbitrary 10 per cent. blending of the 22 billion gallons of gasoline consumed in the United States last year with corn alcohol would require 900 million bushels of corn. Similarly, it would require 800 million bushels of wheat, 3 billion bushels of white potatoes, 2 billion bushels of sweet potatoes or some combination of the four. The present cost of producing corn alcohol gives little hope of immediate production on a large scale for motor fuel. At the present cost of gasoline the corn would have to be available at 25 cents a bushel or less to make corn alcohol in a comparative price class with gasoline. A Department report recommended, however, that replacement fuels should be provided to supplement future decreases in petroleum, even if not needed for a decade.

R. H. O.